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Wu et al.

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(54) **SELECTIVE HYBRID CAPPING LAYER FOR METAL GATES OF TRANSISTORS**

(52) **U.S. Cl.**
CPC .. **H01L 21/76843** (2013.01); **H01L 21/76805** (2013.01); **H01L 29/42376** (2013.01); **H01L 29/785** (2013.01)

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(58) **Field of Classification Search**
CPC H01L 21/76843; H01L 21/76805; H01L 29/42376; H01L 29/785
See application file for complete search history.

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(57) **ABSTRACT**

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A method includes forming a gate electrode on a semiconductor region, recessing the gate electrode to generate a recess, performing a first deposition process to form a first metallic layer on the gate electrode and in the recess, wherein the first deposition process is performed using a first precursor, and performing a second deposition process to form a second metallic layer on the first metallic layer using a second precursor different from the first precursor. The first metallic layer and the second metallic layer comprise a same metal. The method further includes forming a dielectric hard mask over the second metallic layer, and forming a gate contact plug penetrating through the dielectric hard mask. The gate contact plug contacts a top surface of the second metallic layer.

(65) **Prior Publication Data**

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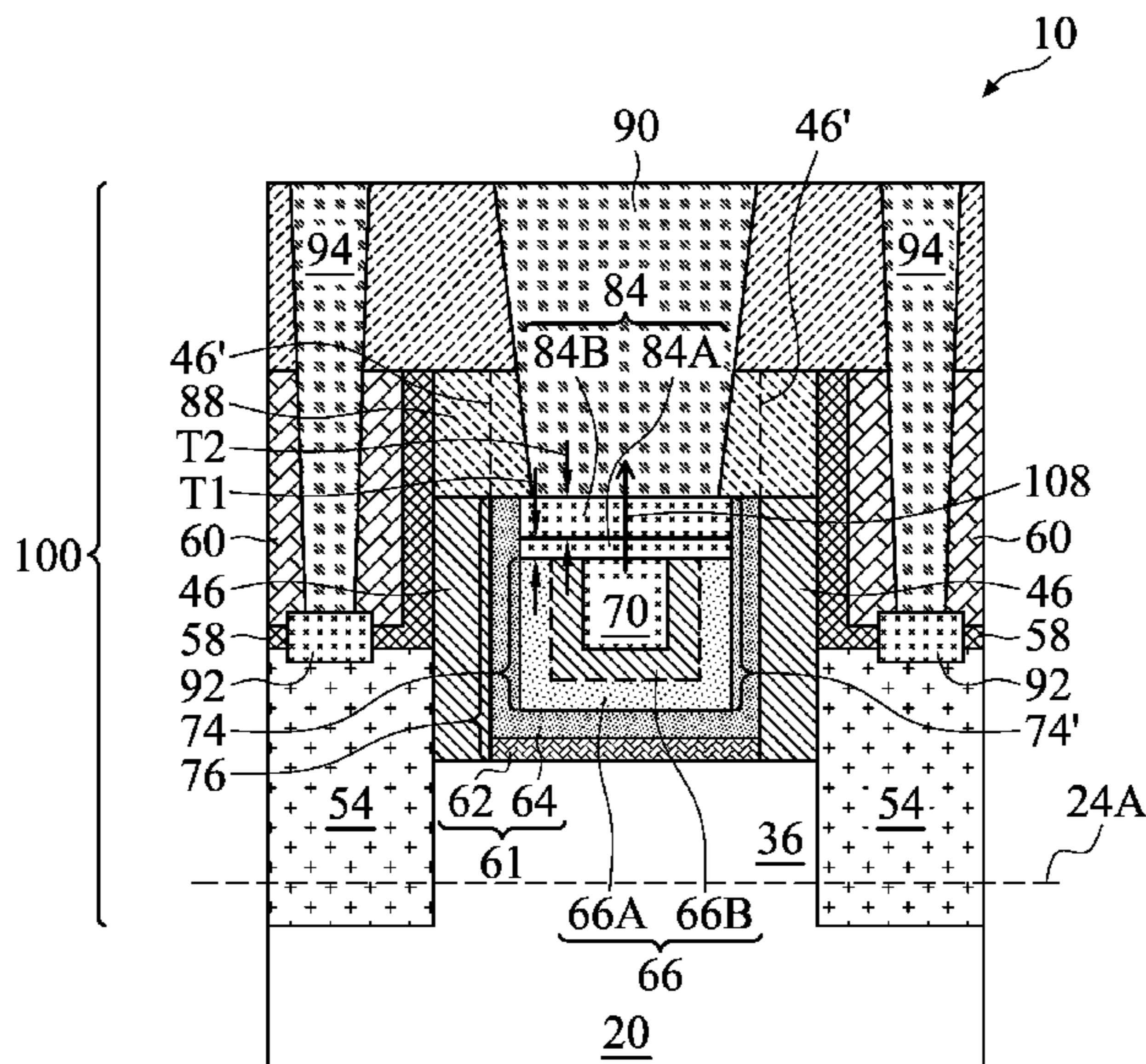
Related U.S. Application Data

(60) Provisional application No. 62/967,872, filed on Jan. 30, 2020.

(51) **Int. Cl.**

H01L 21/768 (2006.01)
H01L 29/78 (2006.01)
H01L 29/423 (2006.01)

20 Claims, 26 Drawing Sheets



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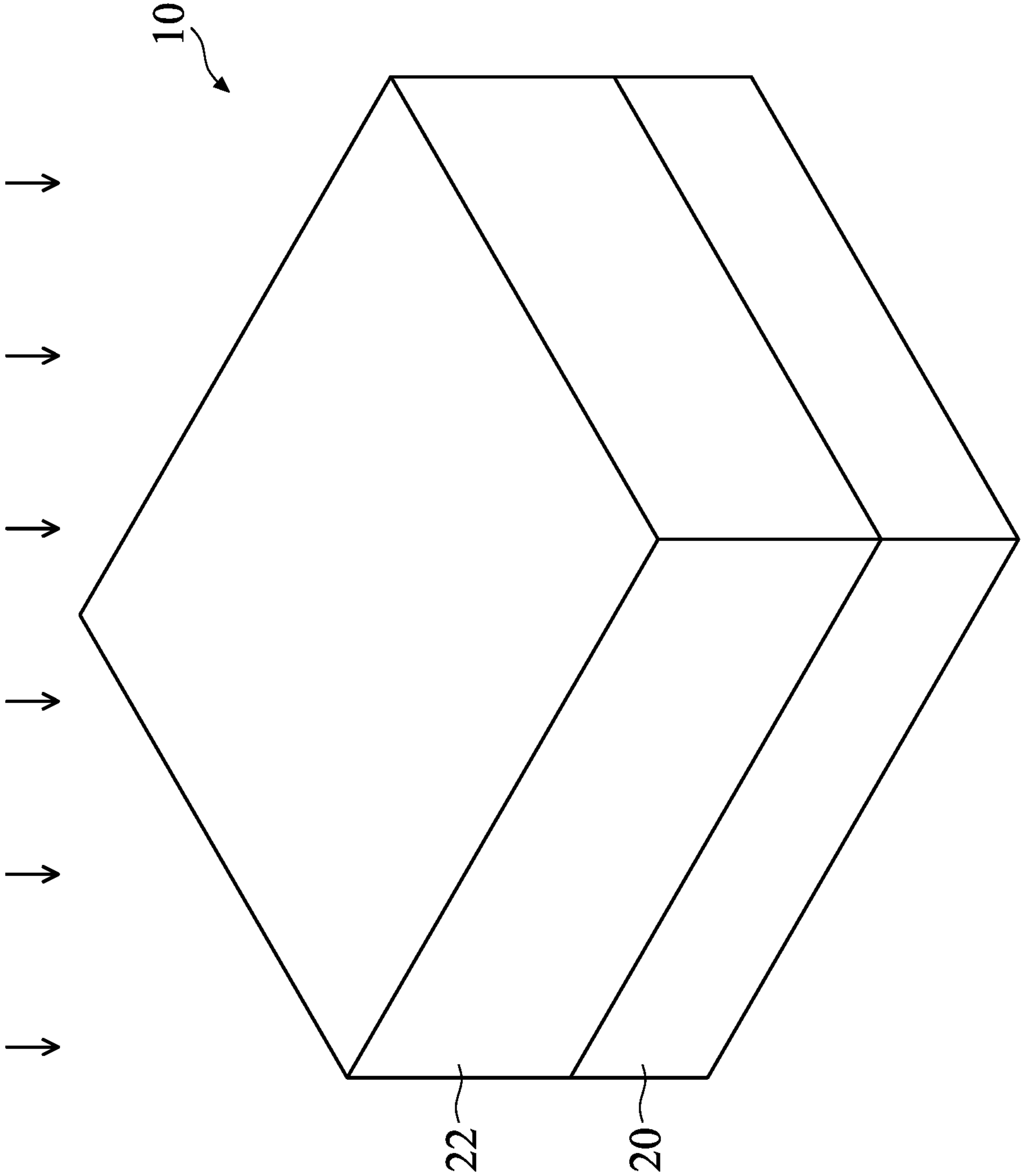
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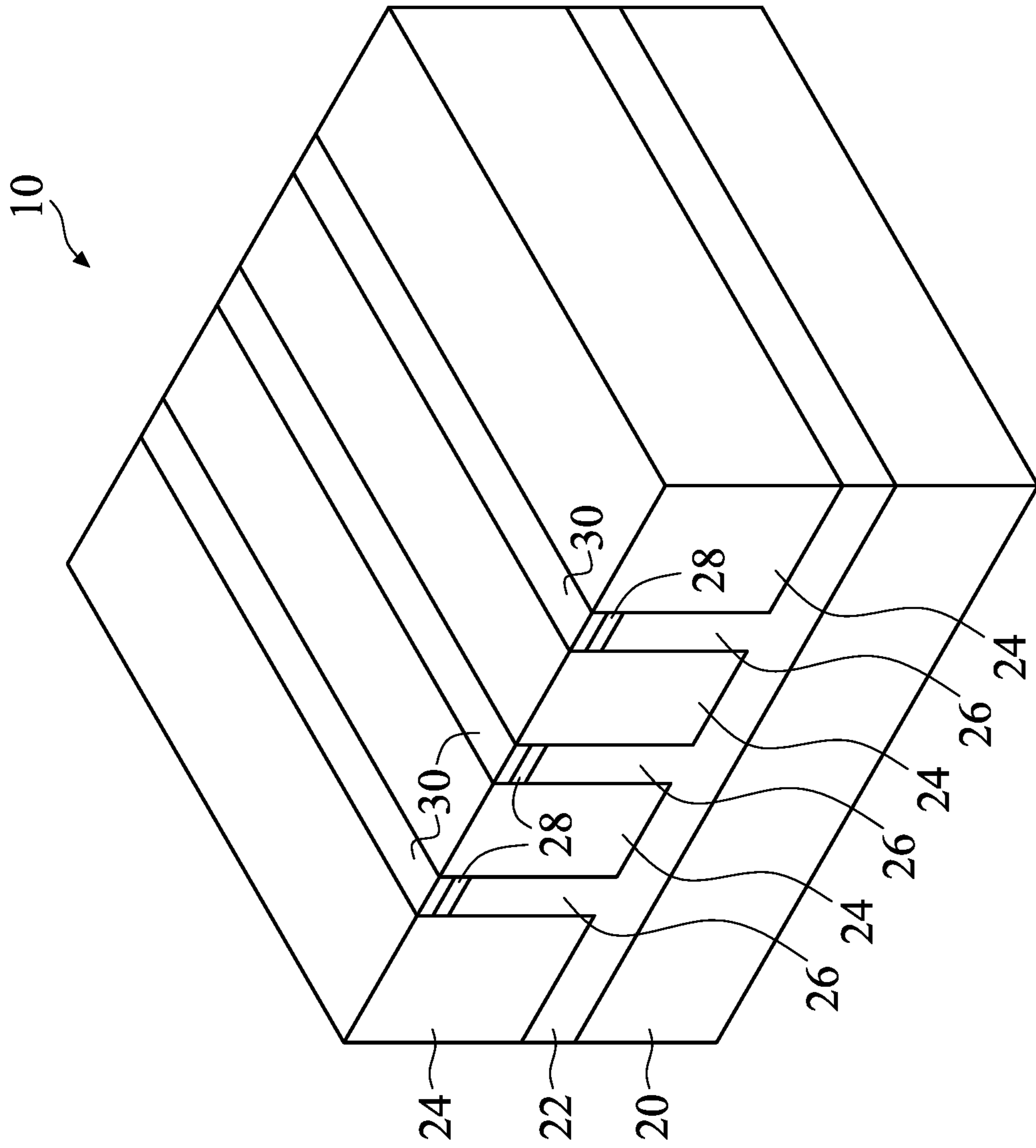


FIG. 2

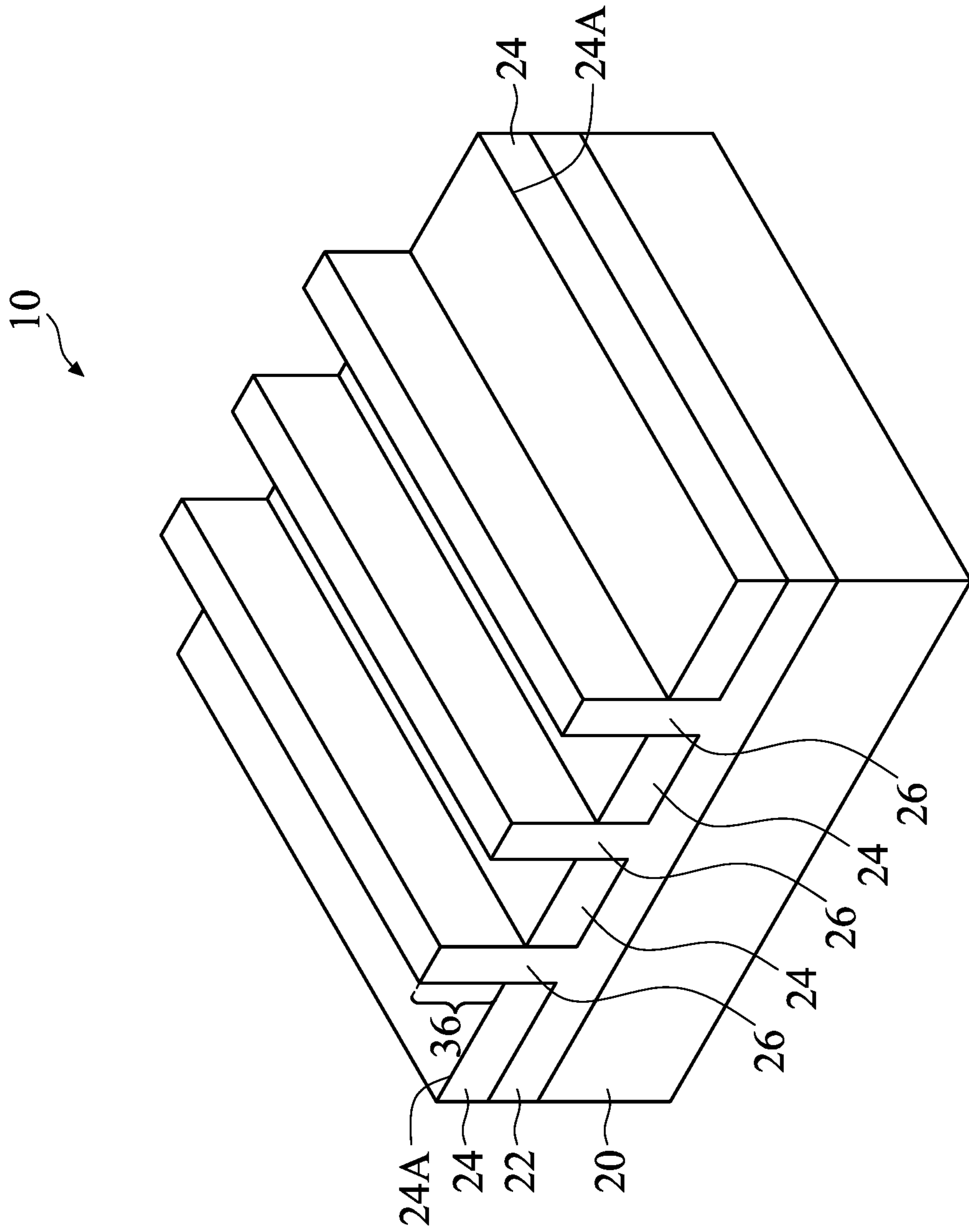


FIG. 3

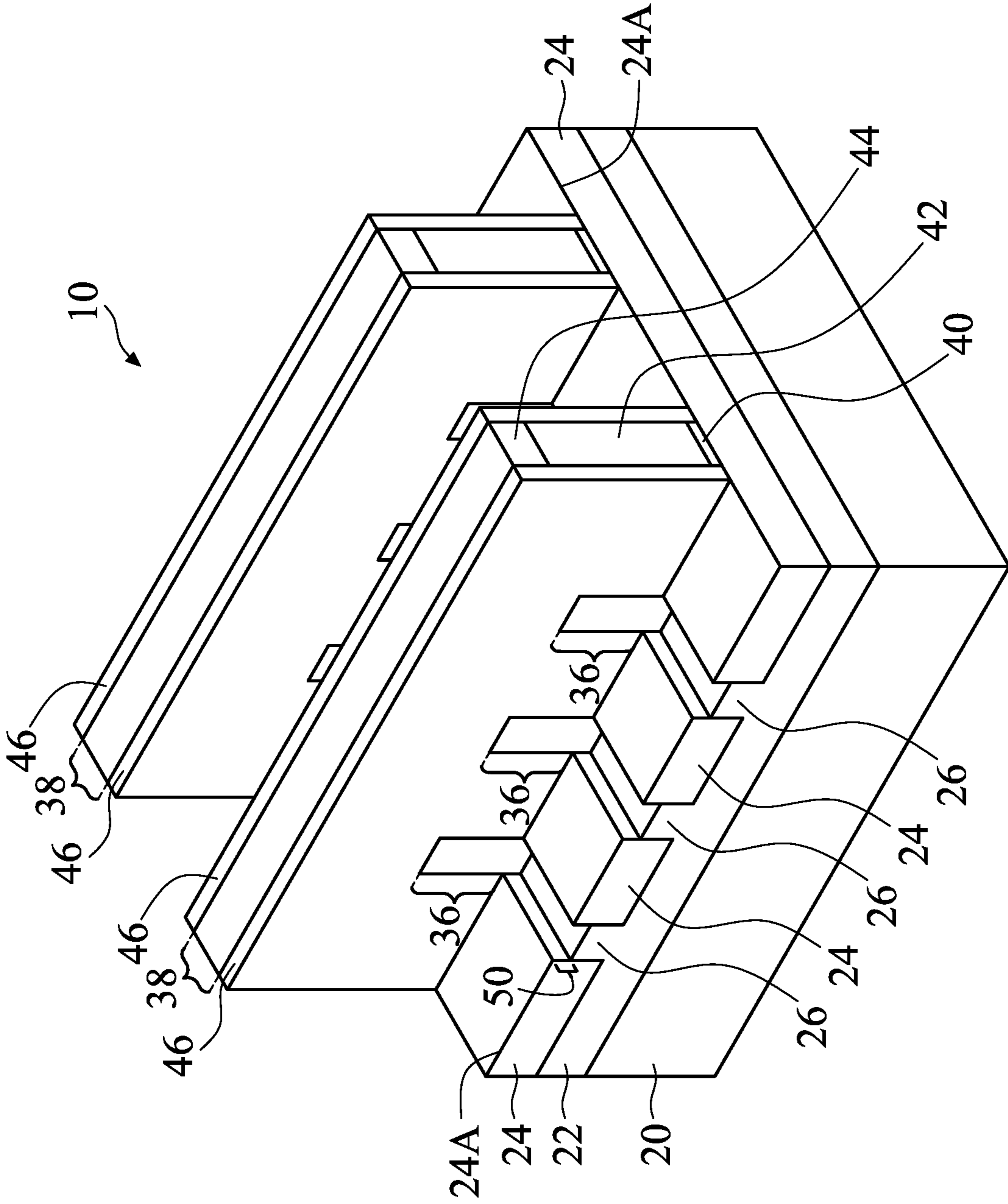


FIG. 5

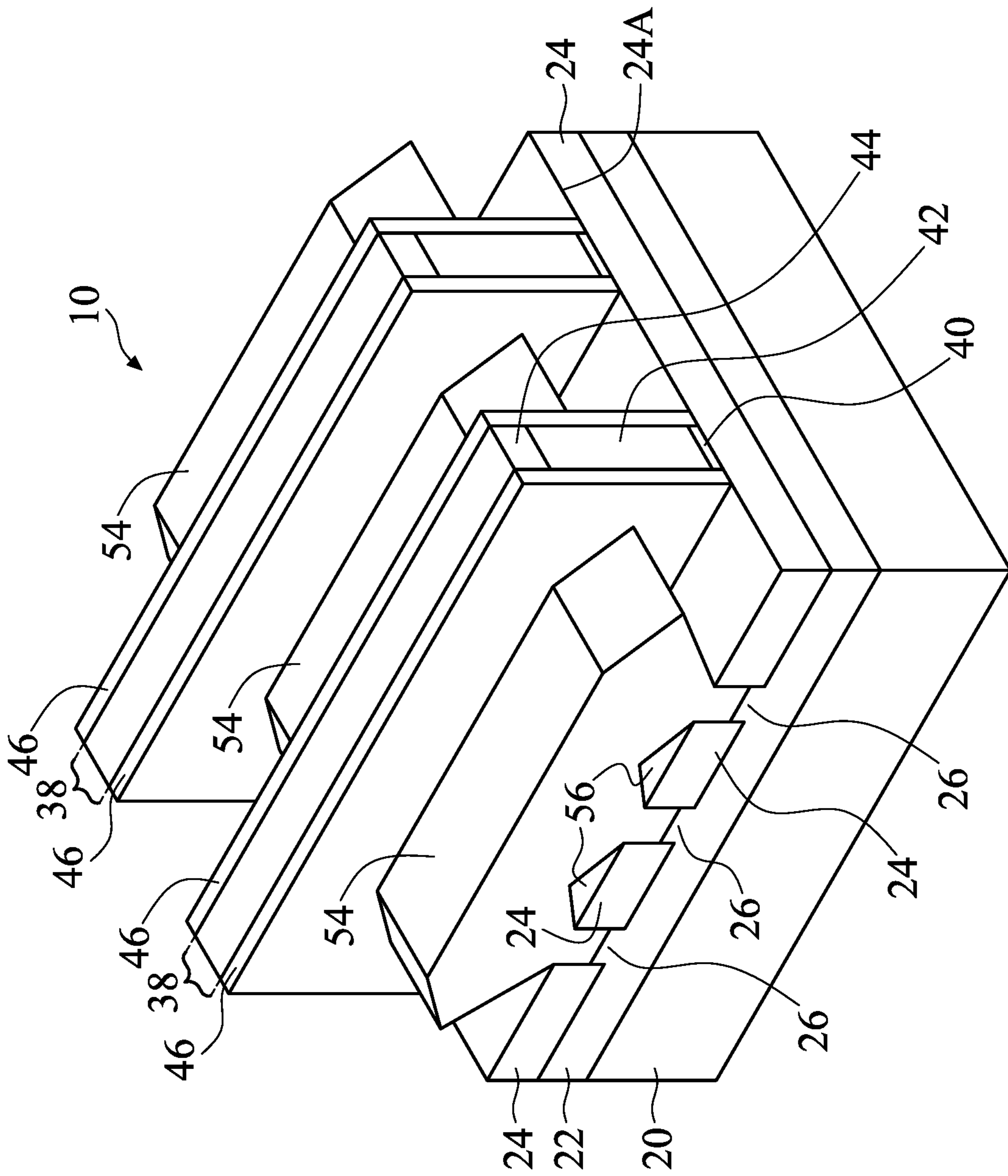


FIG. 6

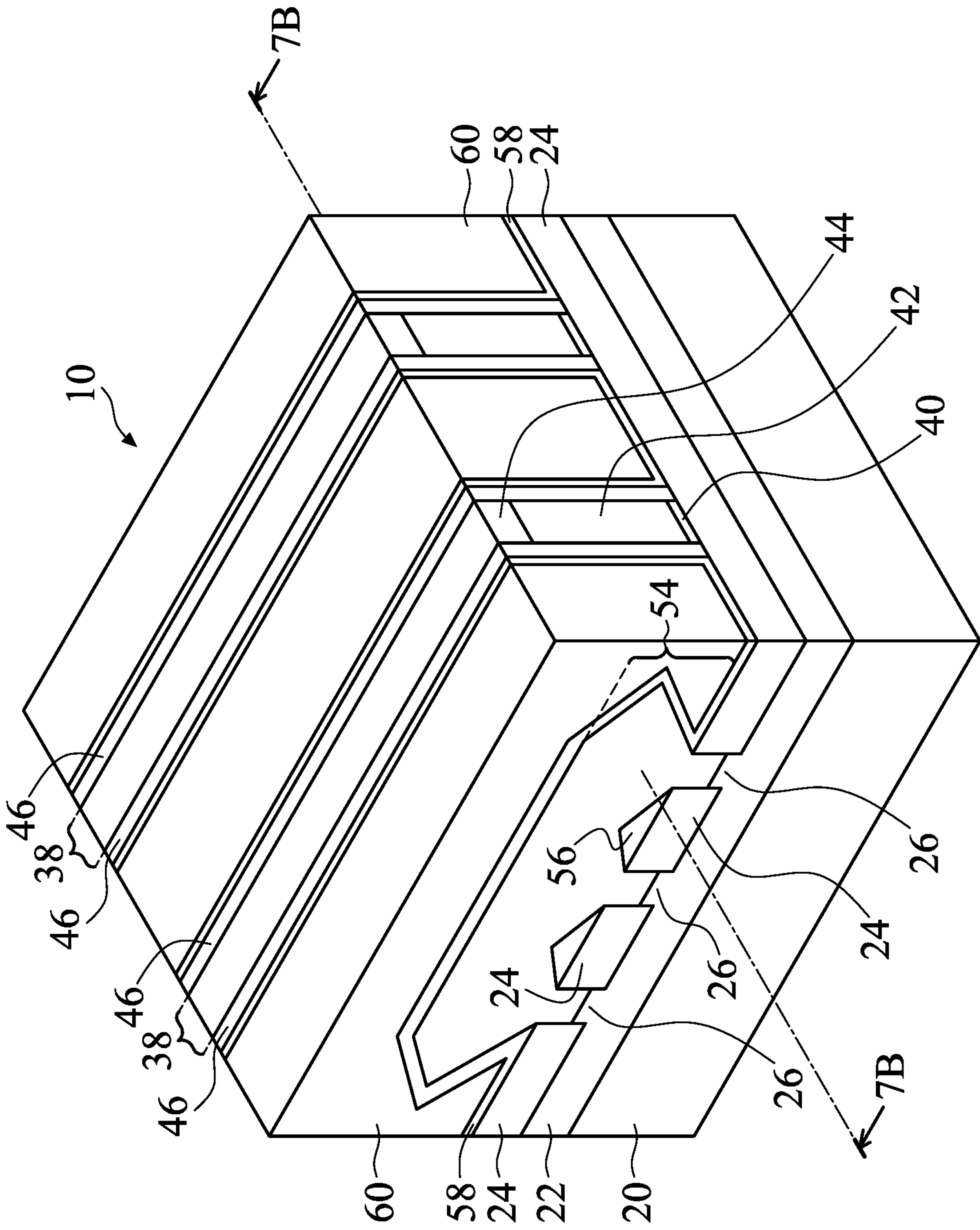


FIG. 7A

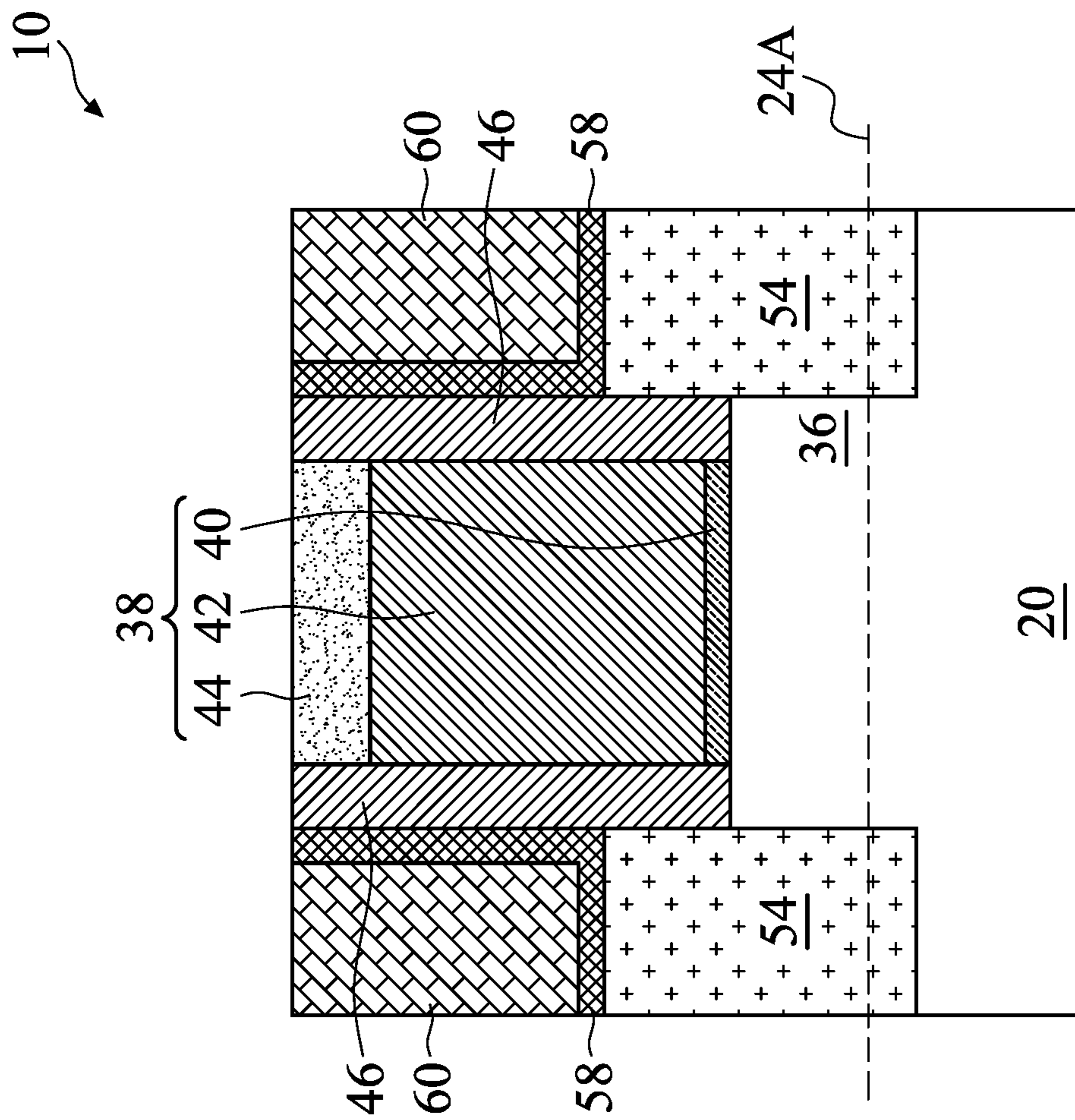


FIG. 7B

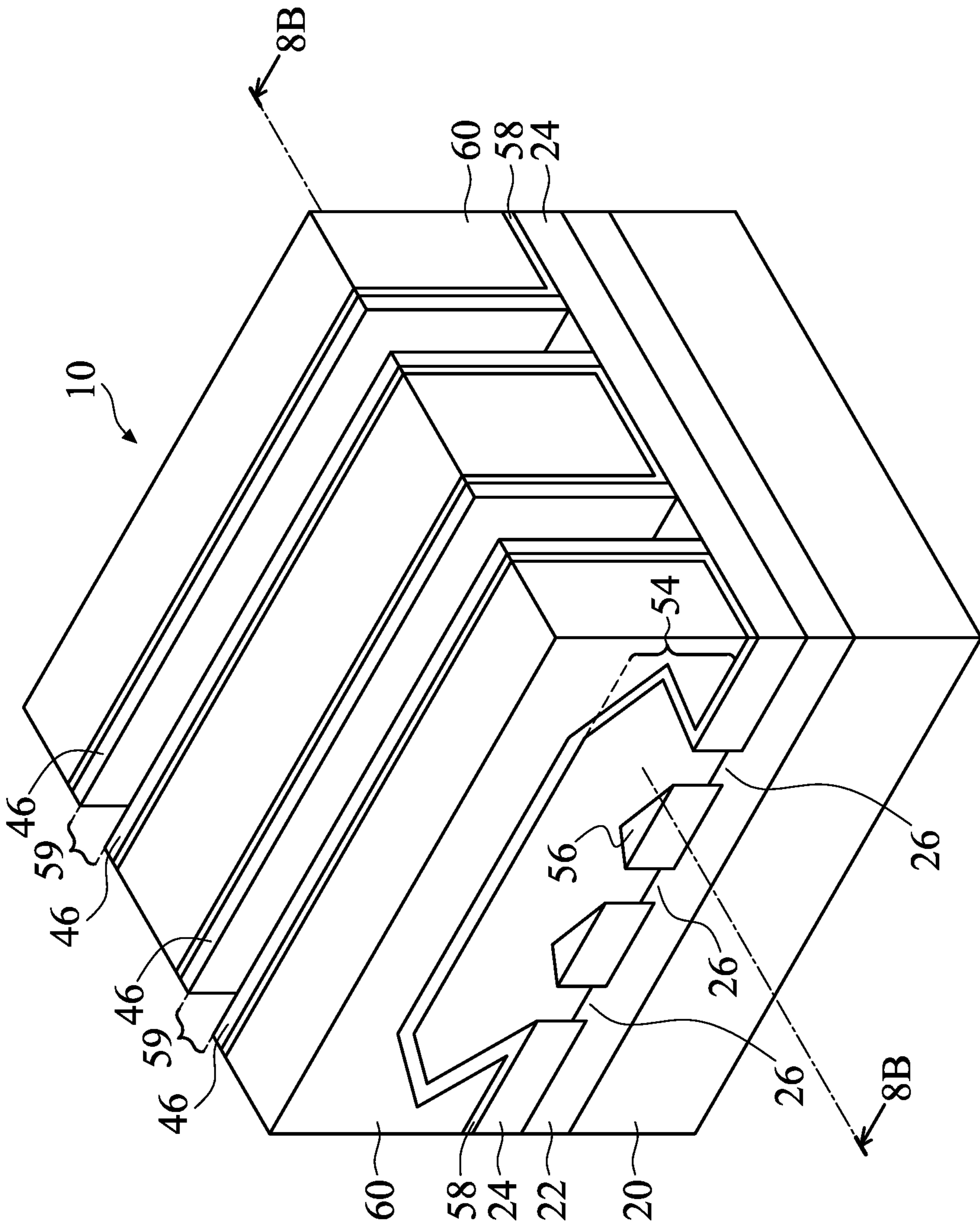


FIG. 8A

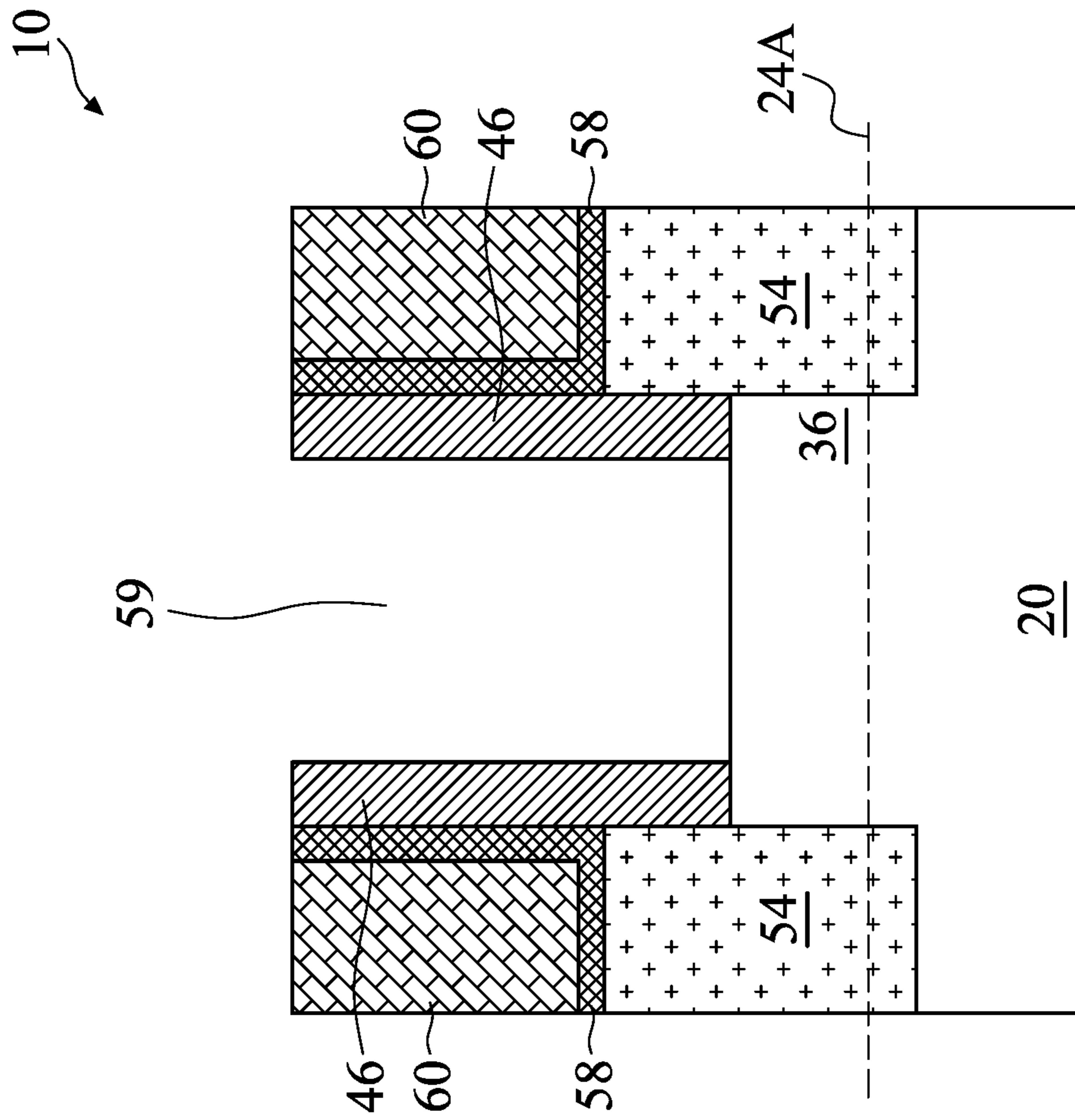


FIG. 8B

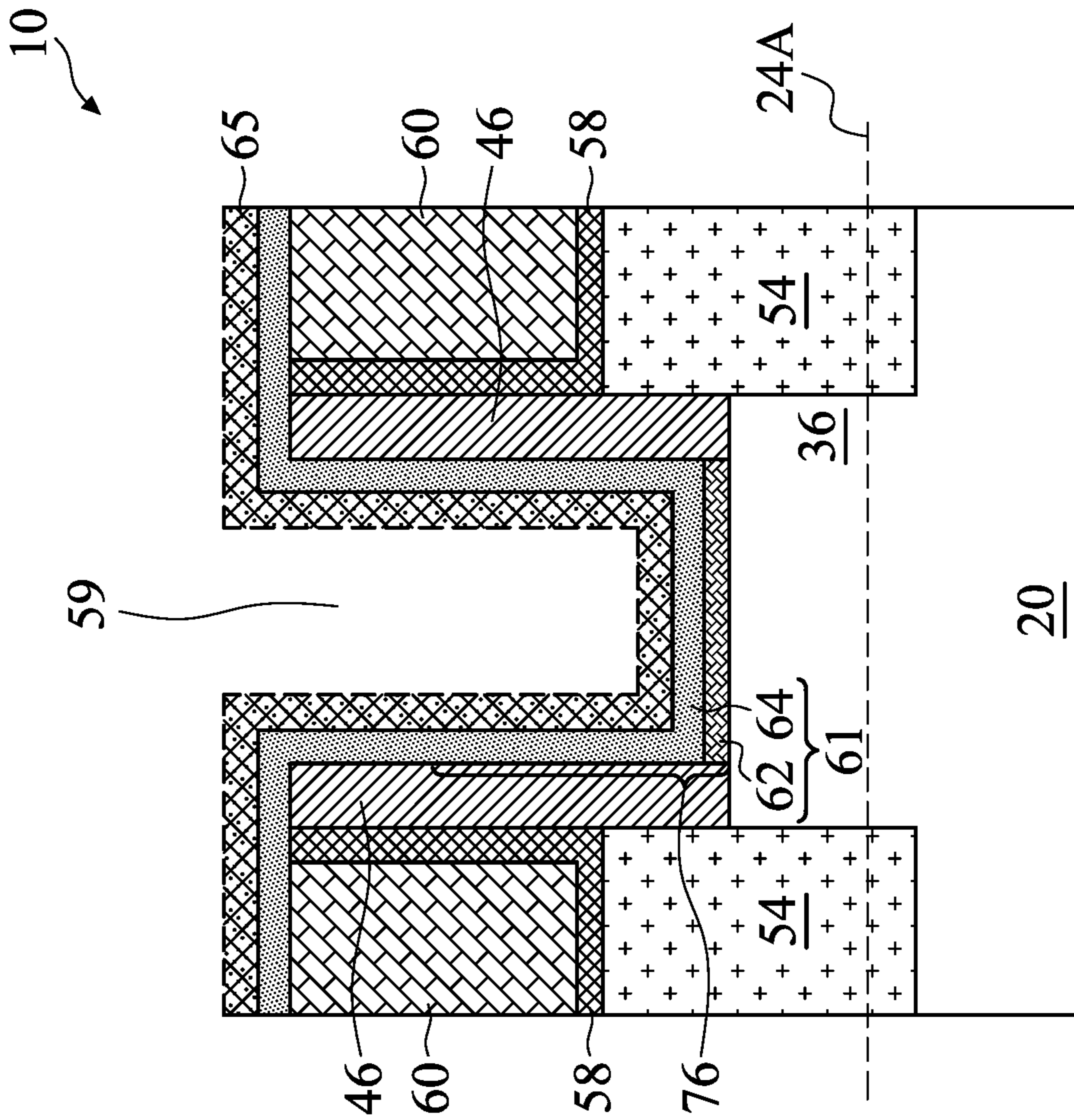


FIG. 9

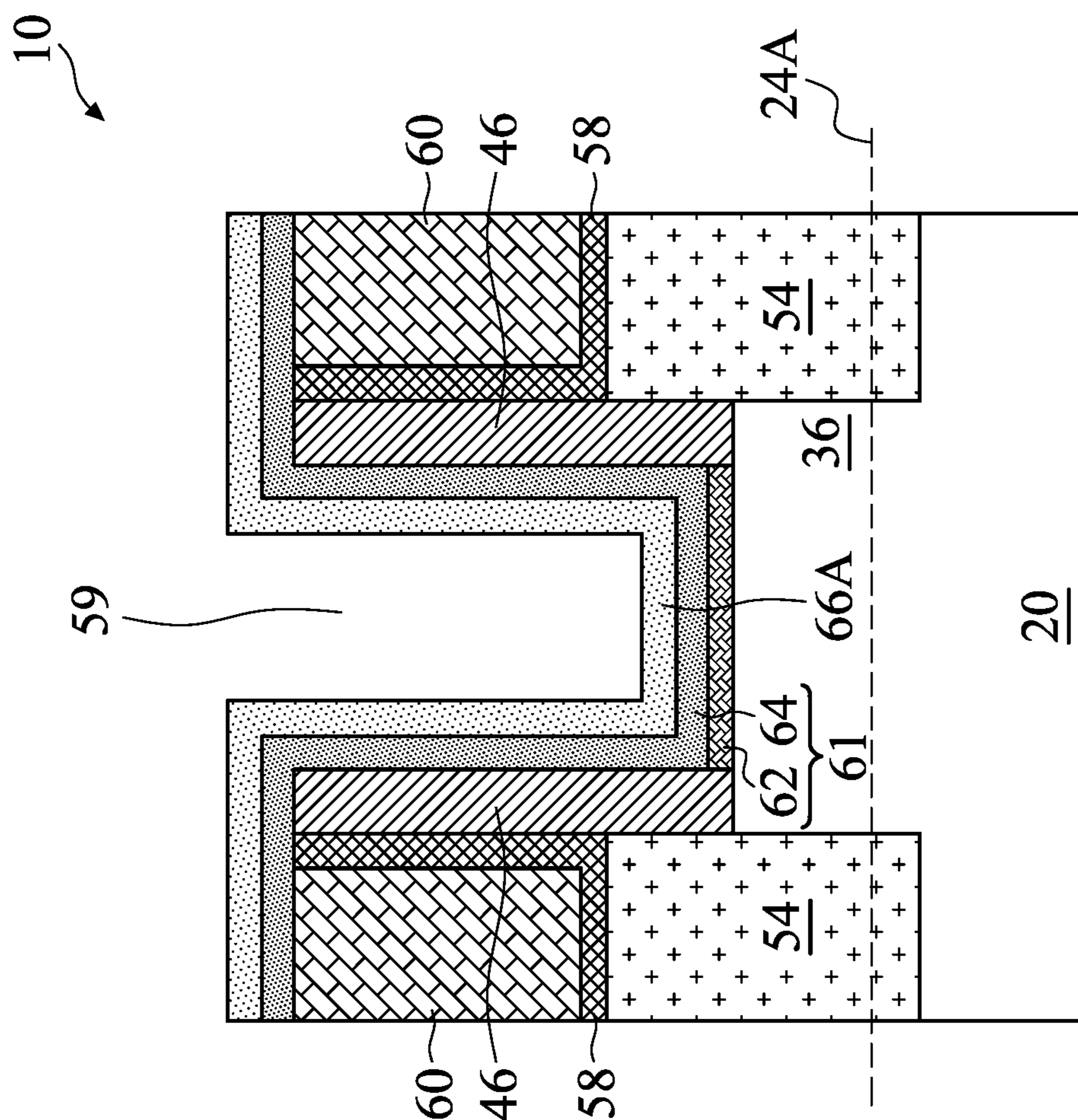


FIG. 10

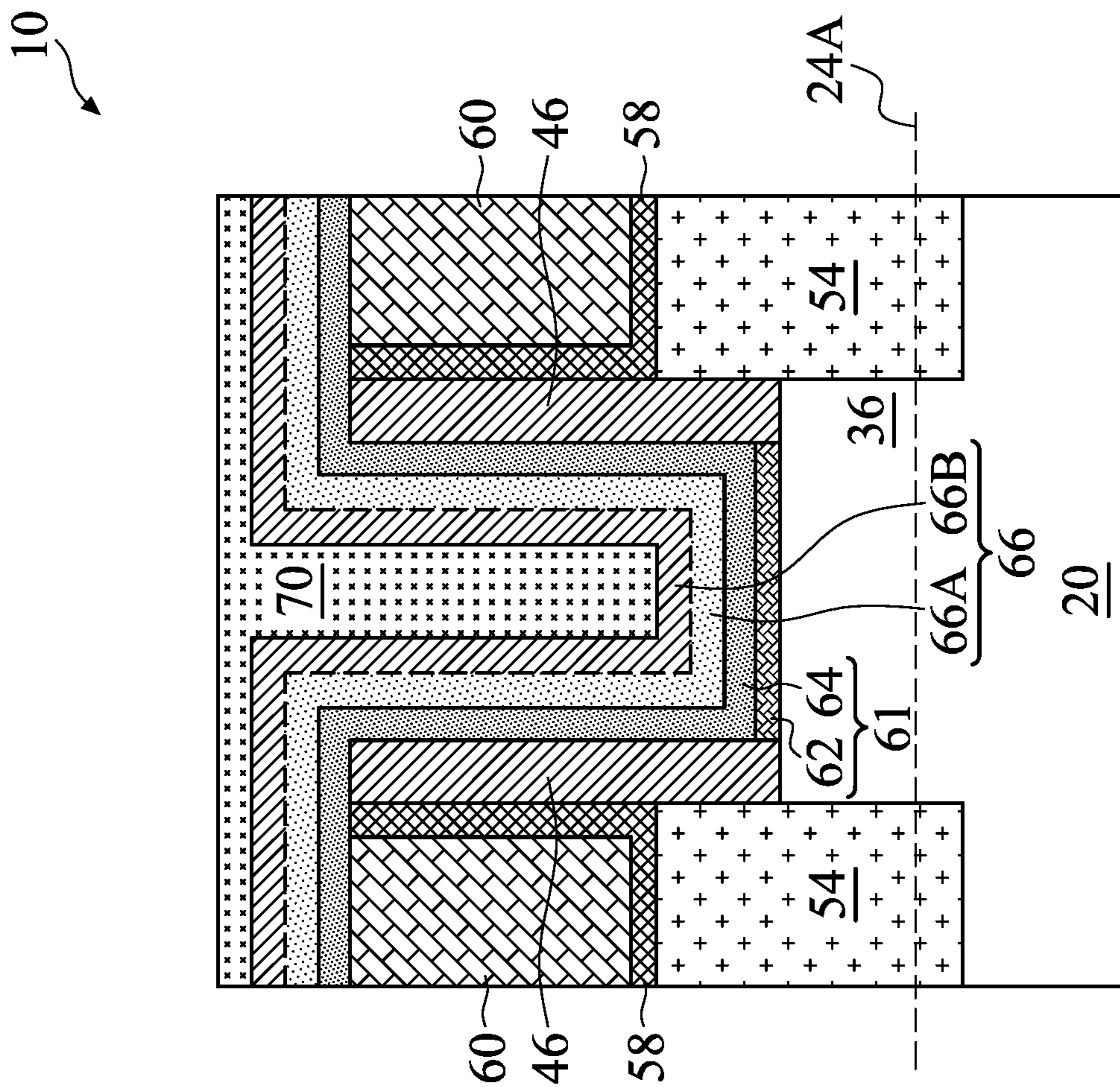


FIG. 11

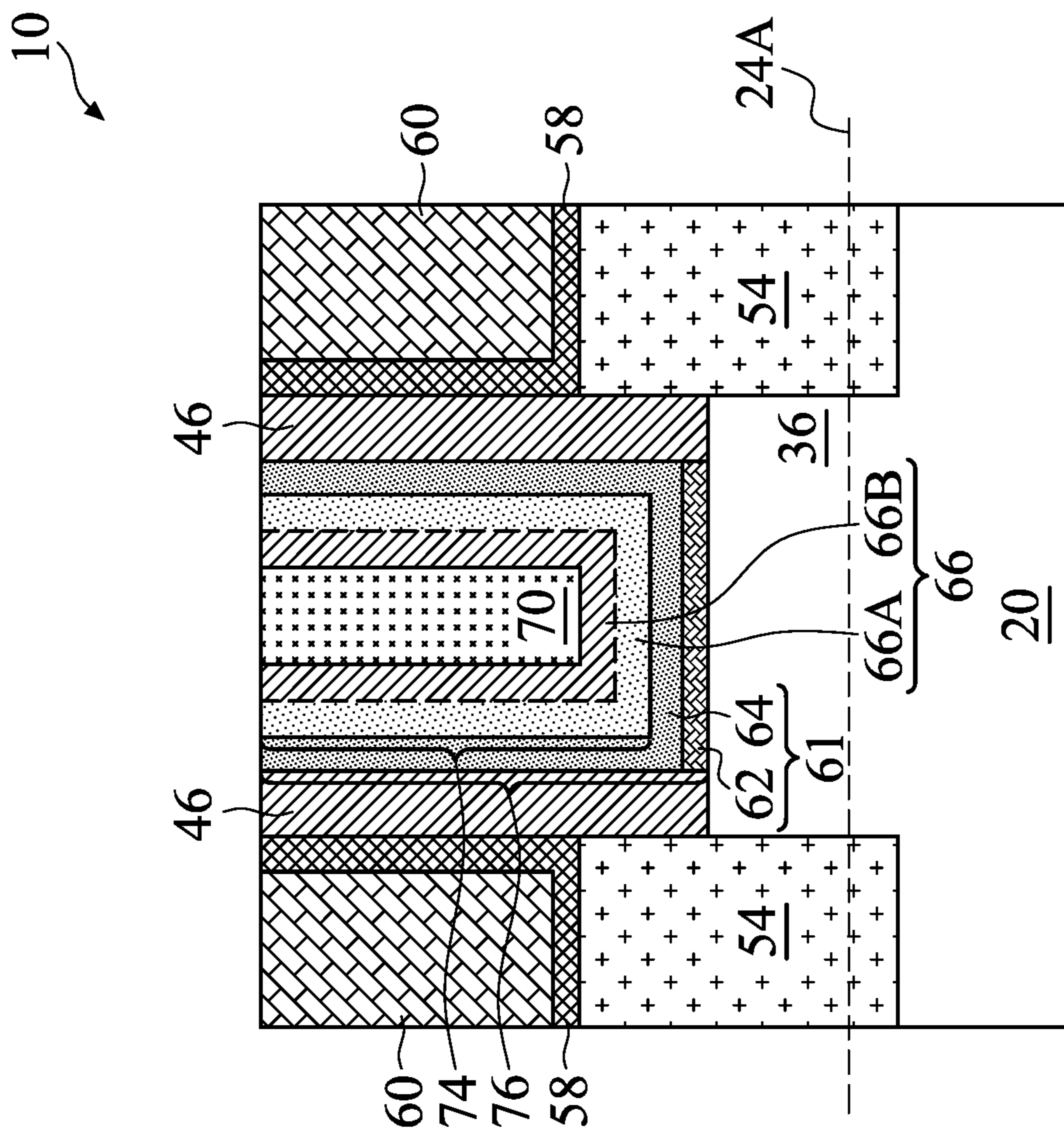


FIG. 12

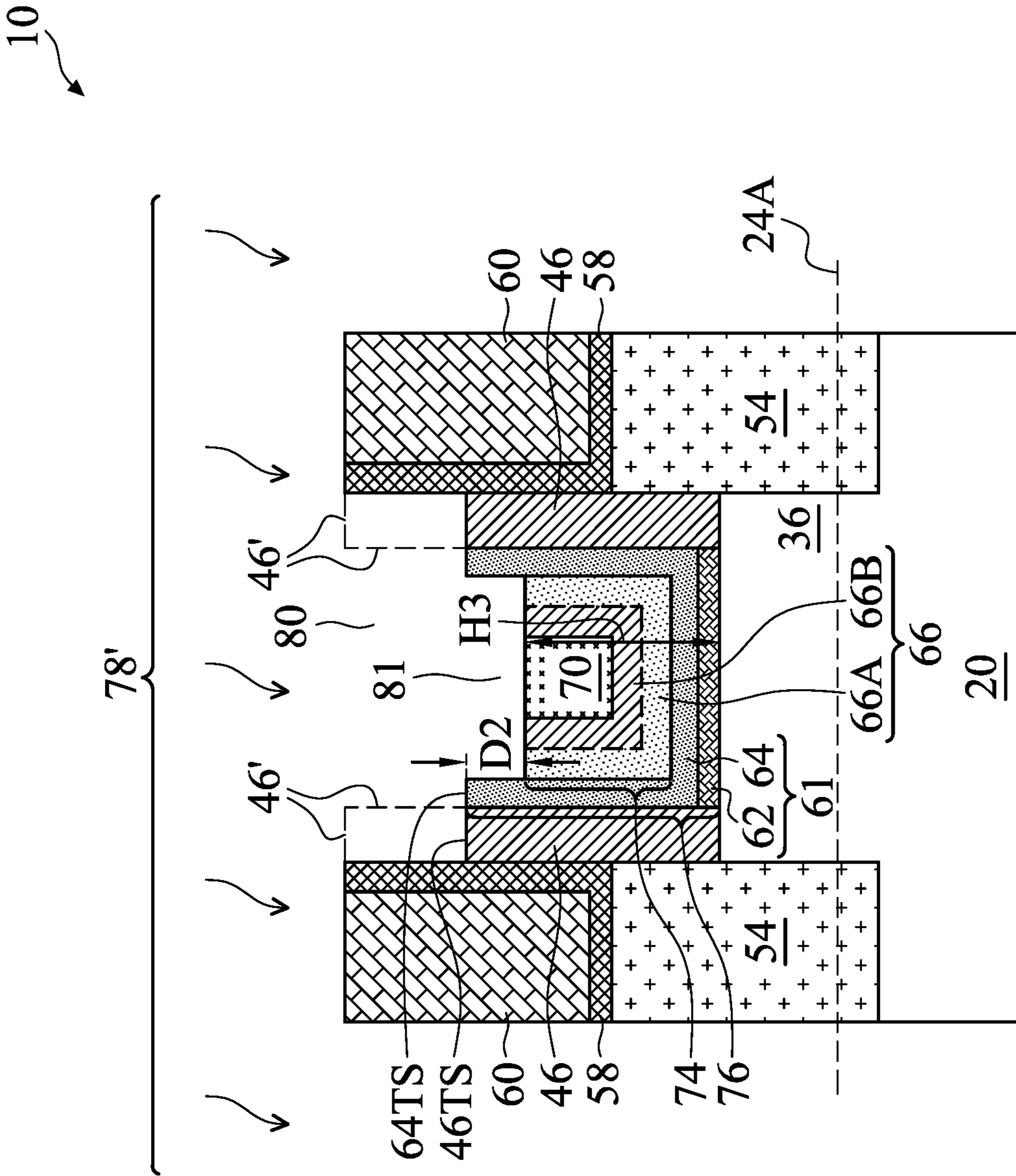


FIG. 14

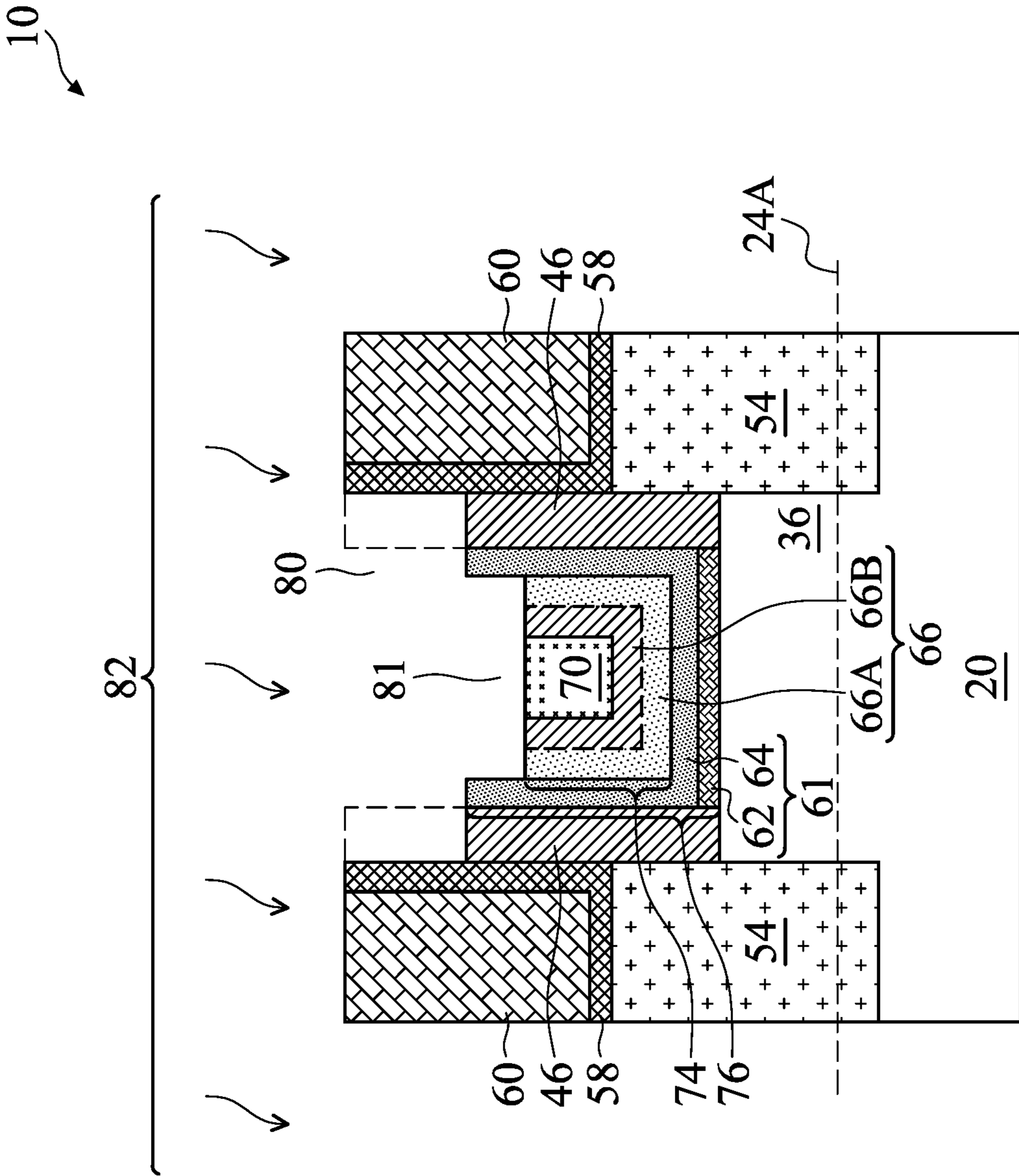


FIG. 15

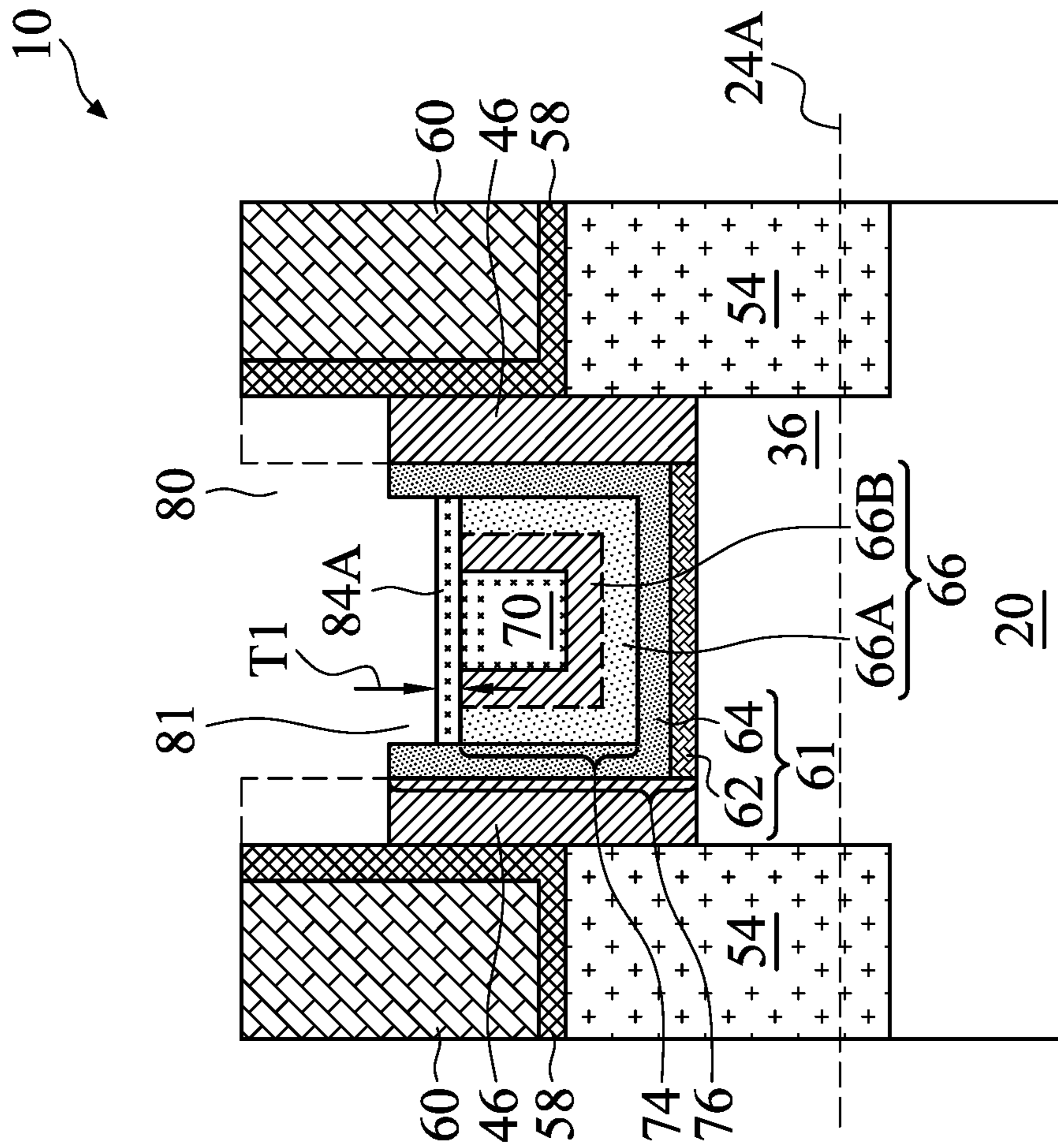


FIG. 16

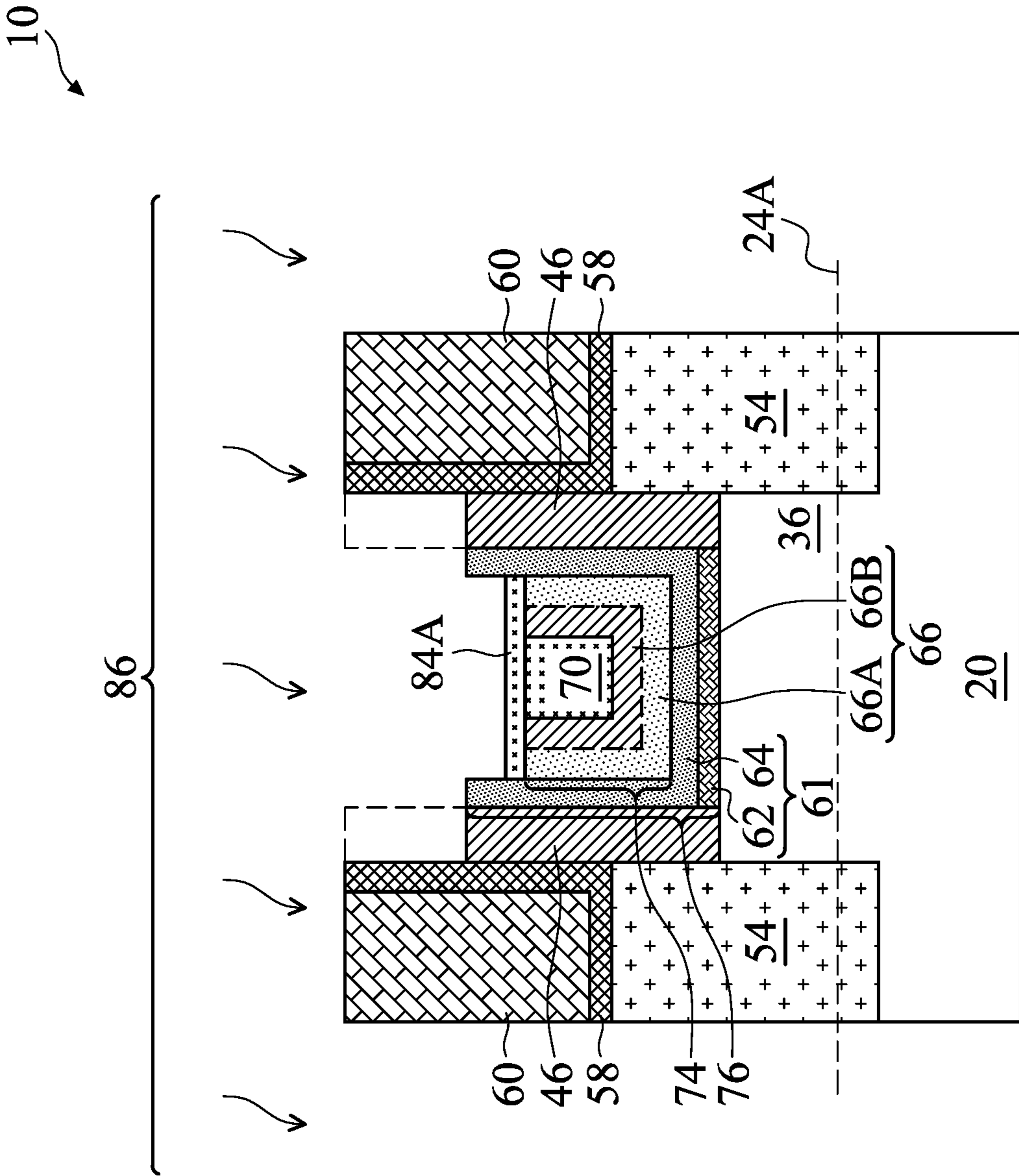


FIG. 17

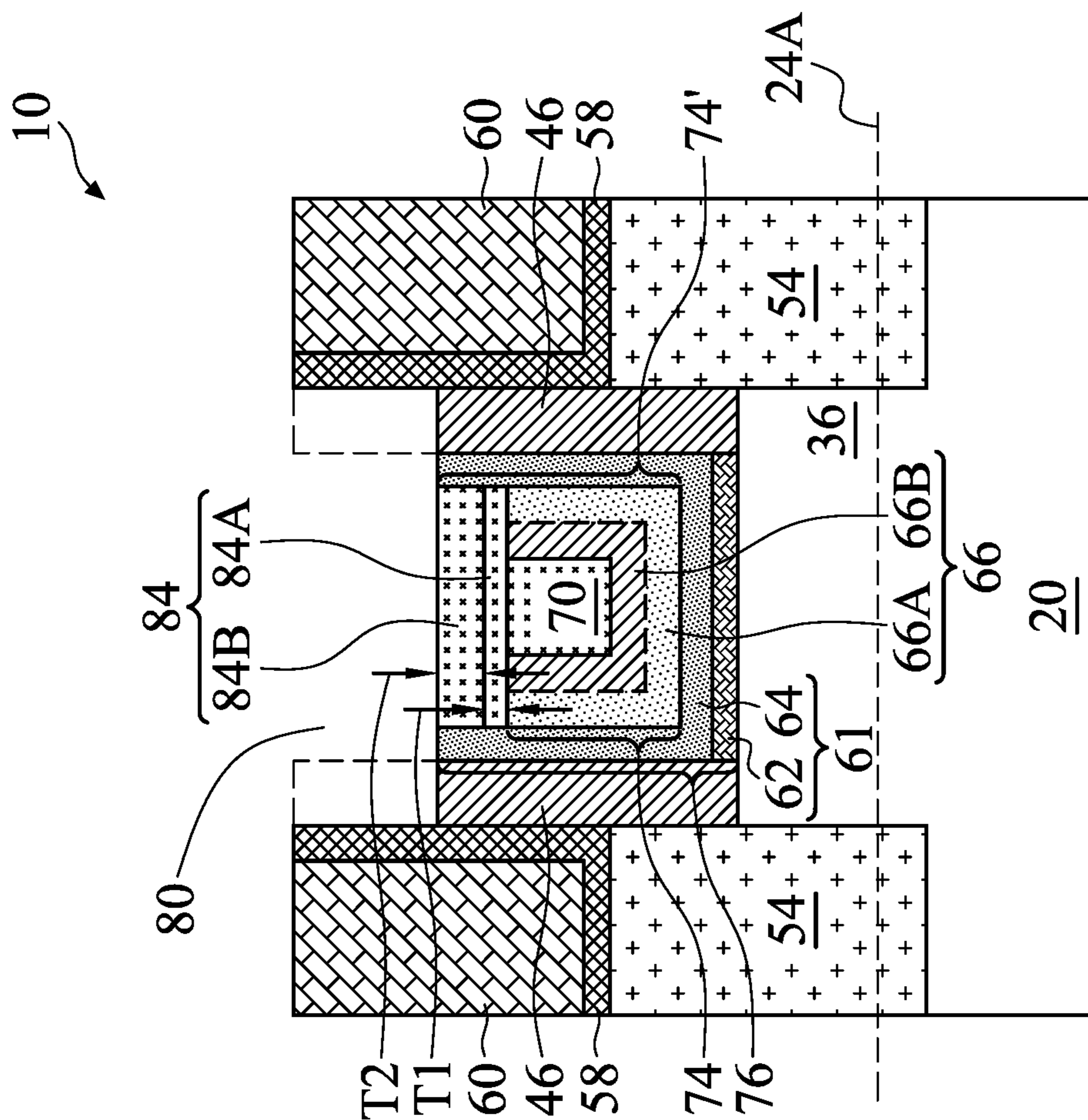


FIG. 18

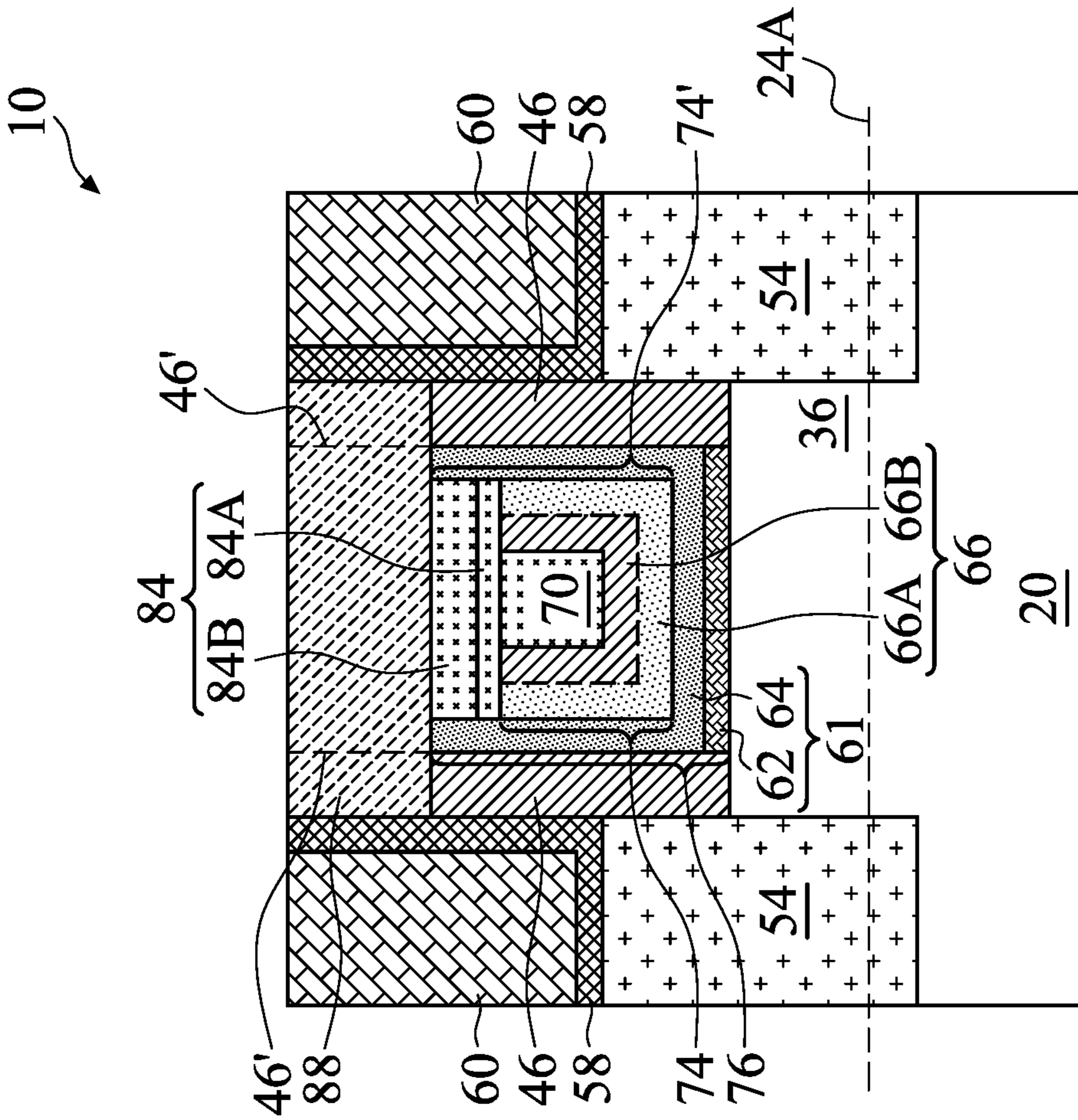


FIG. 19

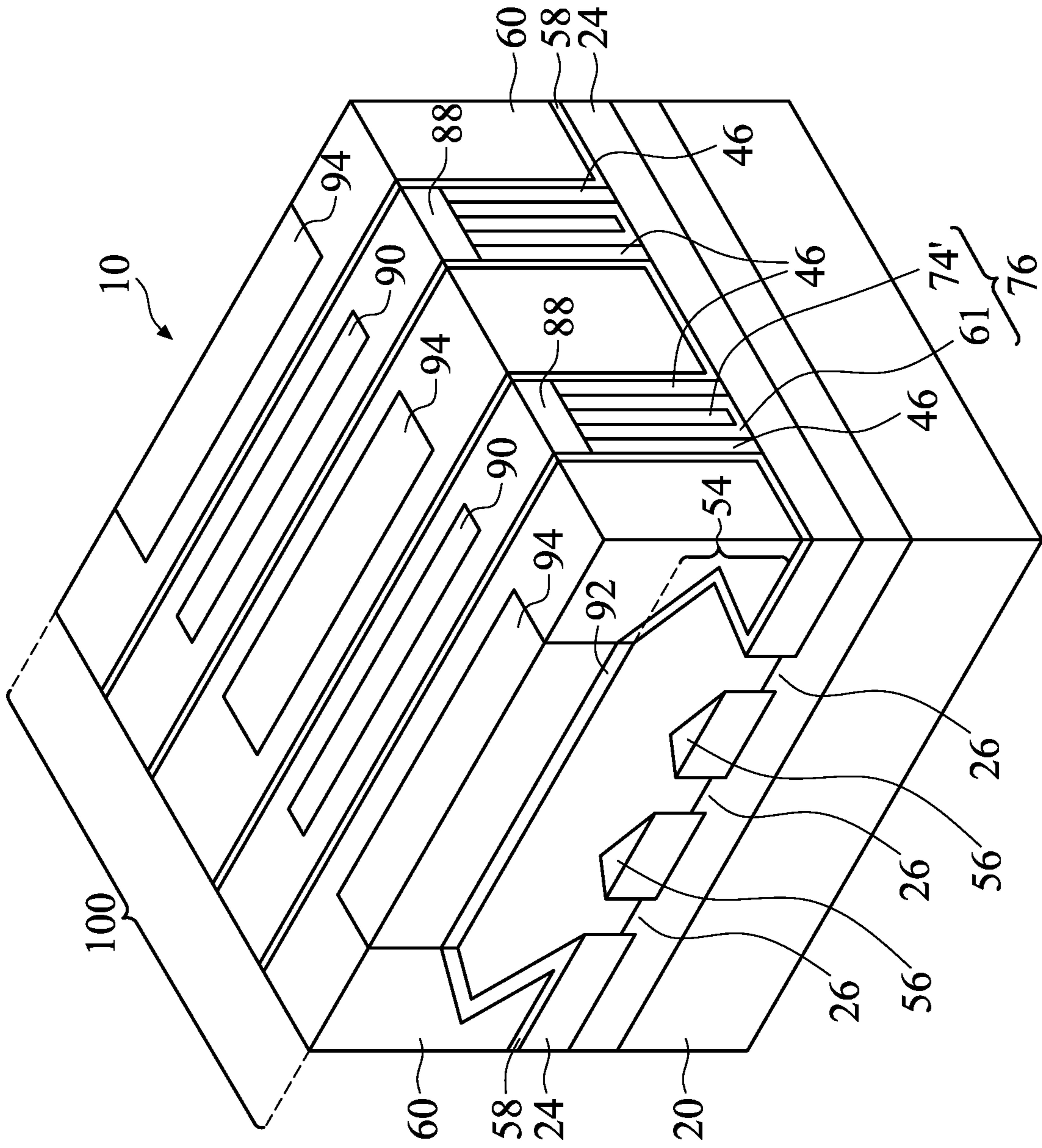


FIG. 20B

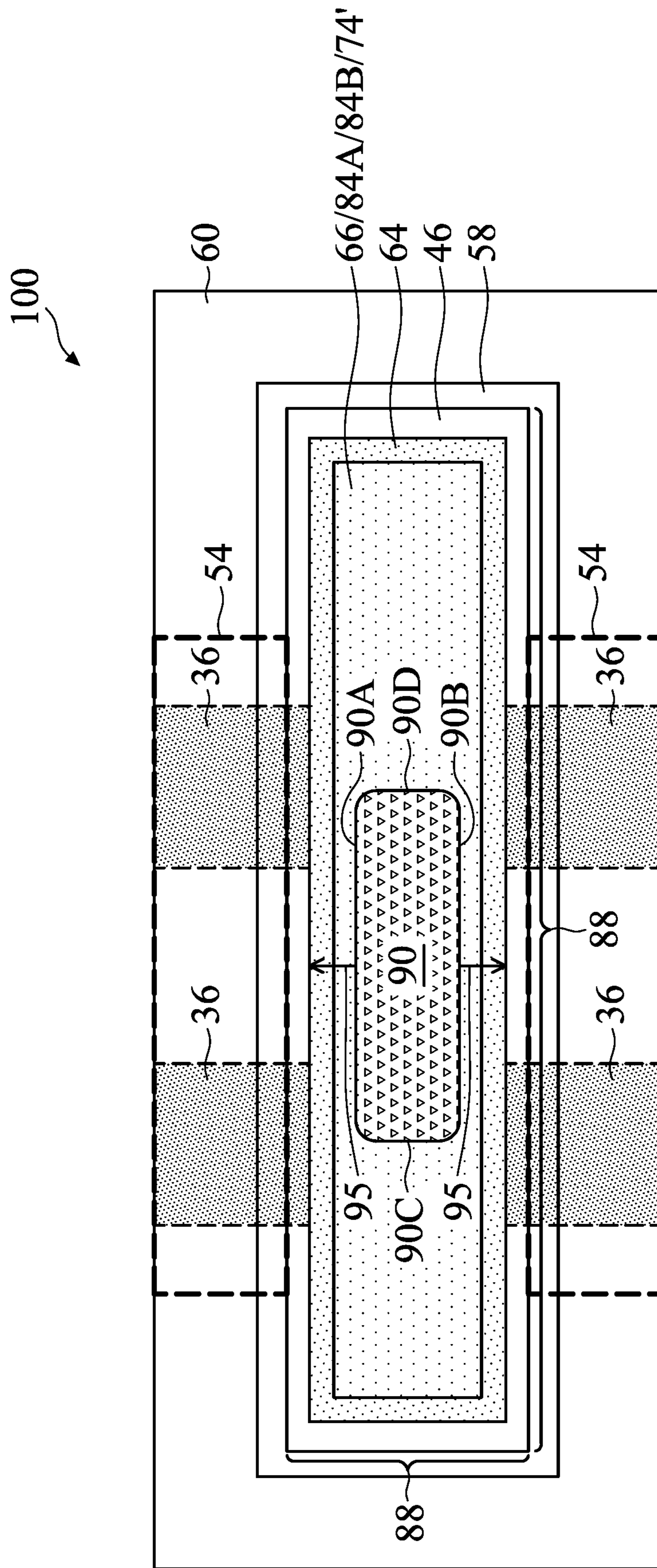


FIG. 21

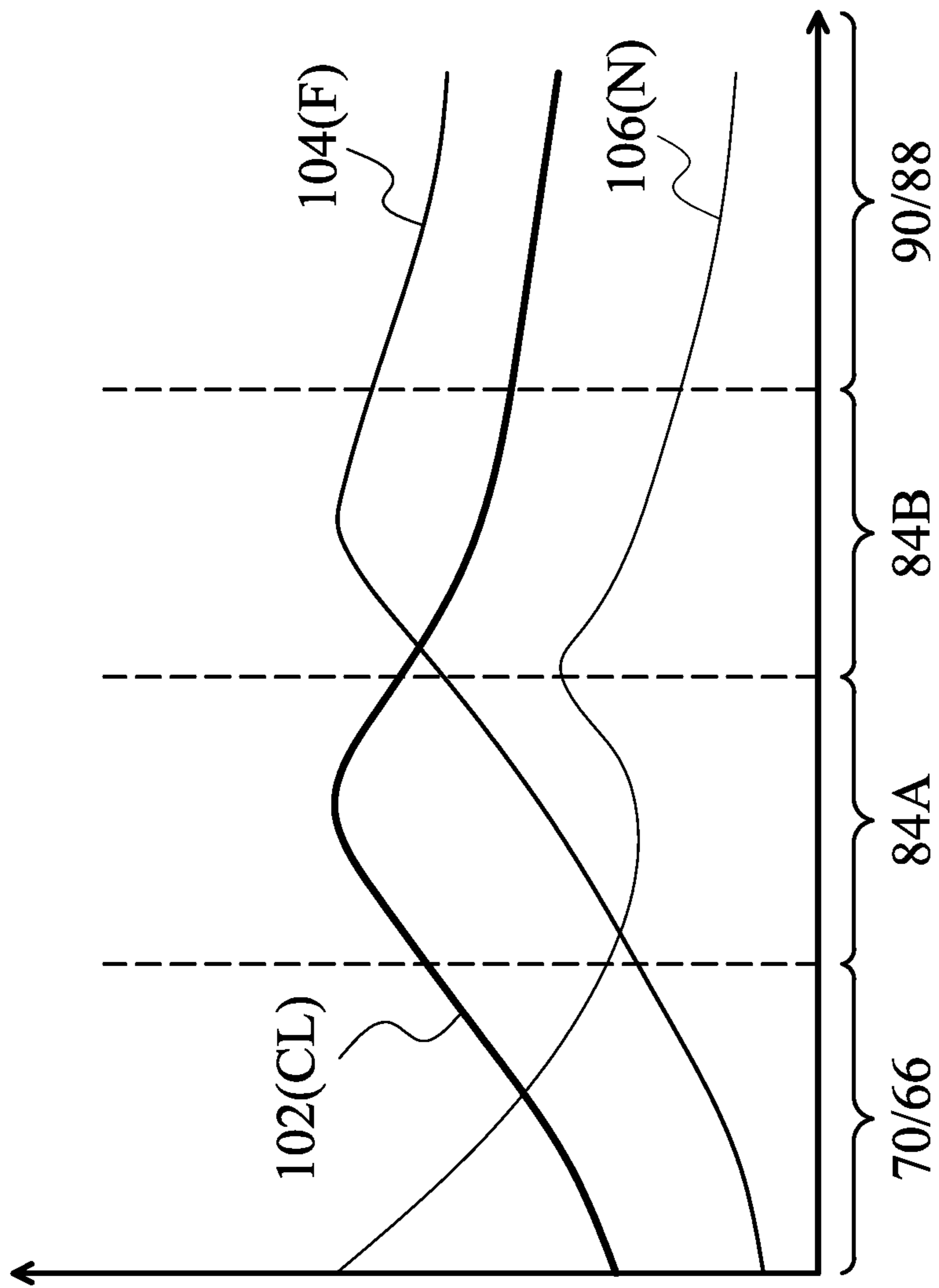


FIG. 22

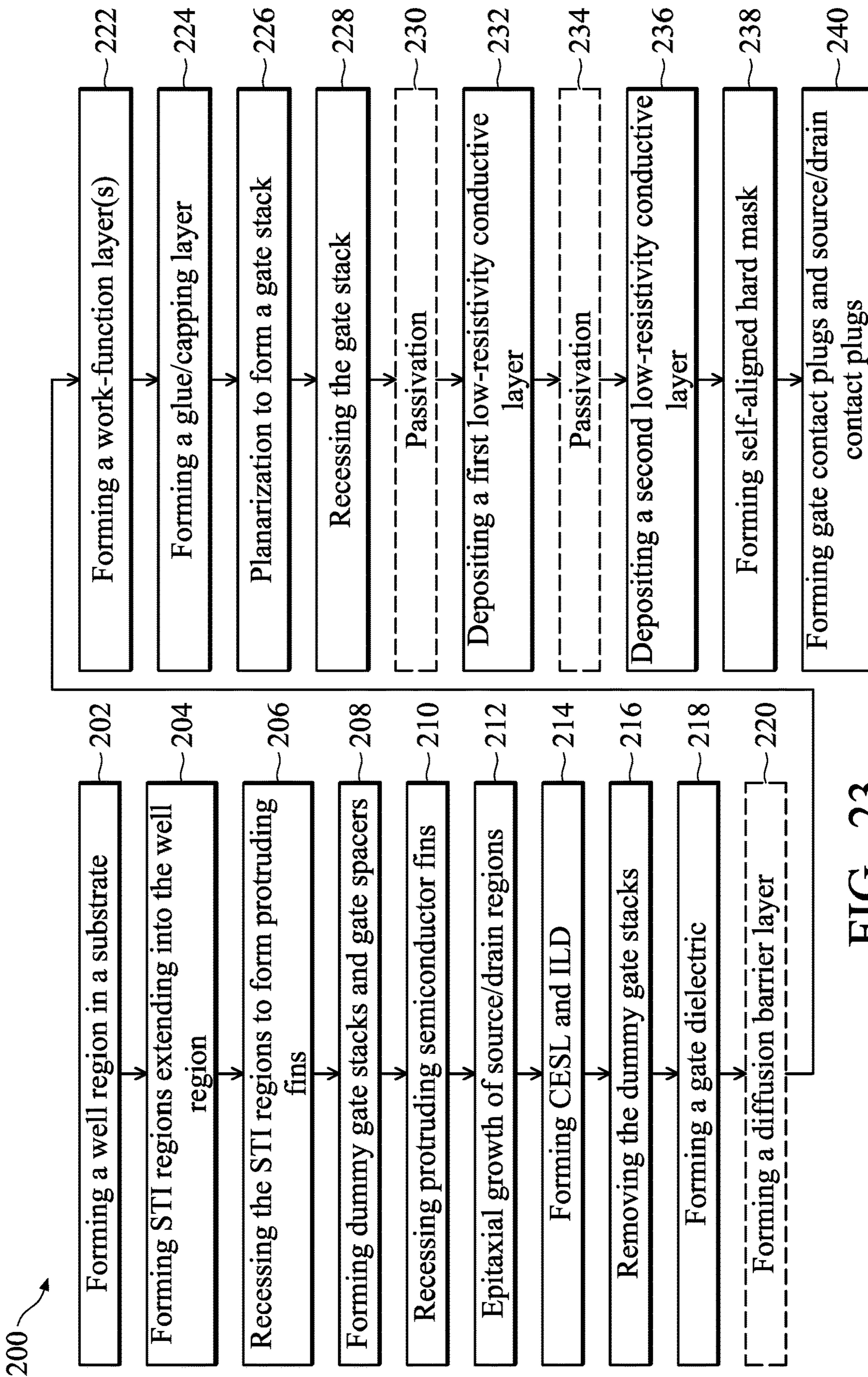


FIG. 23

SELECTIVE HYBRID CAPPING LAYER FOR METAL GATES OF TRANSISTORS

PRIORITY CLAIM AND CROSS-REFERENCE

This application claims the benefit of the f U.S. Provisional Application No. 62/967,872, filed on Jan. 30, 2020, and entitled "Selective Hybrid Capping Layer for Metal Gates of Transistors," which application is hereby incorporated herein by reference.

BACKGROUND

Metal-Oxide-Semiconductor (MOS) devices are basic building elements in integrated circuits. An existing MOS device typically has a gate electrode formed of polysilicon doped with p-type or n-type impurities, using doping operations such as ion implantation or thermal diffusion. The work function of the gate electrode may be adjusted to the band-edge of silicon. For an n-type Metal-Oxide-Semiconductor (NMOS) device, the work function may be adjusted to close to the conduction band of silicon. For a P-type Metal-Oxide-Semiconductor (PMOS) device, the work function may be adjusted to close to the valence band of silicon. Adjusting the work function of the polysilicon gate electrode can be achieved by selecting appropriate impurities.

MOS devices with polysilicon gate electrodes exhibit carrier depletion effect, which is also known as a poly depletion effect. The poly depletion effect occurs when the applied electrical fields sweep away carriers from gate regions close to gate dielectrics, forming depletion layers. In an n-doped polysilicon layer, the depletion layer includes ionized non-mobile donor sites, wherein in a p-doped polysilicon layer, the depletion layer includes ionized non-mobile acceptor sites. The depletion effect results in an increase in the effective gate dielectric thickness, making it more difficult for an inversion layer to be created at the surface of the semiconductor.

The poly depletion problem may be solved by forming metal gate electrodes, wherein the metallic gates used in NMOS devices and PMOS devices may also have band-edge work functions. Accordingly, the resulting metal gates include a plurality of layers to suit to the requirements of the NMOS devices and PMOS devices.

BRIEF DESCRIPTION OF THE DRAWINGS

Aspects of the present disclosure are best understood from the following detailed description when read with the accompanying figures. It is noted that, in accordance with the standard practice in the industry, various features are not drawn to scale. In fact, the dimensions of the various features may be arbitrarily increased or reduced for clarity of discussion.

FIGS. 1-6, 7A, 7B, 8A, 8B, 9-19, 20A, and 20B illustrate the cross-sectional views and perspective views of intermediate stages in the formation of a Fin Field-Effect Transistor (FinFET) in accordance with some embodiments.

FIG. 21 illustrates a plane view of a FinFET in accordance with some embodiments.

FIG. 22 illustrates the distribution of some elements in accordance with some embodiments.

FIG. 23 illustrates a flow chart of a process flow for forming a FinFET in accordance with some embodiments.

DETAILED DESCRIPTION

The following disclosure provides many different embodiments, or examples, for implementing different fea-

tures of the invention. Specific examples of components and arrangements are described below to simplify the present disclosure. These are, of course, merely examples and are not intended to be limiting. For example, the formation of a first feature over or on a second feature in the description that follows may include embodiments in which the first and second features are formed in direct contact, and may also include embodiments in which additional features may be formed between the first and second features, such that the first and second features may not be in direct contact. In addition, the present disclosure may repeat reference numerals and/or letters in the various examples. This repetition is for the purpose of simplicity and clarity and does not in itself dictate a relationship between the various embodiments and/or configurations discussed.

Further, spatially relative terms, such as "underlying," "below," "lower," "overlying," "upper" and the like, may be used herein for ease of description to describe one element or feature's relationship to another element(s) or feature(s) as illustrated in the figures. The spatially relative terms are intended to encompass different orientations of the device in use or operation in addition to the orientation depicted in the figures. The apparatus may be otherwise oriented (rotated 90 degrees or at other orientations) and the spatially relative descriptors used herein may likewise be interpreted accordingly.

Transistors with hybrid capping layers and the methods of forming the same are provided in accordance with some embodiments. A first low-resistivity conductive layer is formed over and contacting the recessed metal gate. The first low-resistivity conductive layer is used as a seed layer, so that a second low-resistivity conductive layer is formed selectively and reaches a desirable thickness. The low-resistivity conductive layers have resistivity values lower than the resistivity values of at least some layers in the metal gate, so that the overall gate resistance of the metal gate is reduced. The intermediate stages of forming the transistors are illustrated in accordance with some embodiments. Some variations of some embodiments are discussed. Throughout the various views and illustrative embodiments, like reference numbers are used to designate like elements. Although method embodiments may be discussed as being performed in a particular order, other method embodiments may be performed in any logical order. In accordance with embodiments, the formation of Fin Field-Effect Transistors (FinFETs) is used as an example to explain the concept of the present disclosure. Other types of transistors such as planar transistors may also adopt the concept of the present disclosure. In accordance with some embodiments of the present disclosure, a metal (replacement) gate is formed for a FinFET. The metal gate is then etched and recessed, so that a recess is generated.

FIGS. 1-6, 7A, 7B, 8A, 8B, 9-19, 20A, and 20B illustrate the cross-sectional views and perspective views of intermediate stages in the formation of FinFETs in accordance with some embodiments of the present disclosure. The processes shown in these figures are also reflected schematically in the process flow 200 shown in FIG. 23.

Referring to FIG. 1, substrate 20 is provided. The substrate 20 may be a semiconductor substrate, such as a bulk semiconductor substrate, a Semiconductor-On-Insulator (SOI) substrate, or the like, which may be doped (e.g., with a p-type or an n-type dopant) or undoped. The semiconductor substrate 20 may be a part of wafer 10, such as a silicon wafer. Generally, an SOI substrate is a layer of a semiconductor material formed on an insulator layer. The insulator layer may be, for example, a Buried Oxide (BOX) layer, a

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silicon oxide layer, or the like. The insulator layer is provided on a substrate, typically a silicon or glass substrate. Other substrates such as a multi-layered or gradient substrate may also be used. In some embodiments, the semiconductor material of semiconductor substrate **20** may include silicon; germanium; a compound semiconductor including carbon-doped silicon, gallium arsenic, gallium phosphide, indium phosphide, indium arsenide, and/or indium antimonide; an alloy semiconductor including SiGe, GaAsP, AlInAs, AlGaAs, GaInAs, GaInP, and/or GaInAsP; or combinations thereof.

Further referring to FIG. 1, well region **22** is formed in substrate **20**. The respective process is illustrated as process **202** in the process flow **200** shown in FIG. **23**. In accordance with some embodiments of the present disclosure, well region **22** is a p-type well region formed through implanting a p-type impurity, which may be boron, indium, or the like, into substrate **20**. In accordance with other embodiments of the present disclosure, well region **22** is an n-type well region formed through implanting an n-type impurity, which may be phosphorus, arsenic, antimony, or the like, into substrate **20**. The resulting well region **22** may extend to the top surface of substrate **20**. The n-type or p-type impurity concentration may be equal to or less than 10^{18} cm^{-3} , such as in the range between about 10^{17} cm^{-3} and about 10^{18} cm^{-3} .

Referring to FIG. 2, isolation regions **24** are formed to extend from a top surface of substrate **20** into substrate **20**. Isolation regions **24** are alternatively referred to as Shallow Trench Isolation (STI) regions hereinafter. The respective process is illustrated as process **204** in the process flow **200** shown in FIG. **23**. The portions of substrate **20** between neighboring STI regions **24** are referred to as semiconductor strips **26**. To form STI regions **24**, pad oxide layer **28** and hard mask layer **30** are formed on semiconductor substrate **20**, and are then patterned. Pad oxide layer **28** may be a thin film formed of silicon oxide. In accordance with some embodiments of the present disclosure, pad oxide layer **28** is formed in a thermal oxidation process, wherein a top surface layer of semiconductor substrate **20** is oxidized. Pad oxide layer **28** acts as an adhesion layer between semiconductor substrate **20** and hard mask layer **30**. Pad oxide layer **28** may also act as an etch stop layer for etching hard mask layer **30**. In accordance with some embodiments of the present disclosure, hard mask layer **30** is formed of silicon nitride, for example, using Low-Pressure Chemical Vapor Deposition (LPCVD). In accordance with other embodiments of the present disclosure, hard mask layer **30** is formed by thermal nitridation of silicon, or Plasma Enhanced Chemical Vapor Deposition (PECVD). A photo resist (not shown) is formed on hard mask layer **30** and is then patterned. Hard mask layer **30** is then patterned using the patterned photo resist as an etching mask to form hard masks **30** as shown in FIG. 2.

Next, the patterned hard mask layer **30** is used as an etching mask to etch pad oxide layer **28** and substrate **20**, followed by filling the resulting trenches in substrate **20** with a dielectric material(s). A planarization process such as a Chemical Mechanical Polish (CMP) process or a mechanical grinding process is performed to remove excessing portions of the dielectric materials, and the remaining portions of the dielectric materials(s) are STI regions **24**. STI regions **24** may include a liner dielectric (not shown), which may be a thermal oxide formed through a thermal oxidation of a surface layer of substrate **20**. The liner dielectric may also be a deposited silicon oxide layer, silicon nitride layer, or the like formed using, for example, Atomic Layer Deposition (ALD), High-Density Plasma Chemical Vapor Deposition

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(HDPCVD), or Chemical Vapor Deposition (CVD). STI regions **24** may also include a dielectric material over the liner oxide, wherein the dielectric material may be formed using Flowable Chemical Vapor Deposition (FCVD), spin-on coating, or the like. The dielectric material over the liner dielectric may include silicon oxide in accordance with some embodiments.

The top surfaces of hard masks **30** and the top surfaces of STI regions **24** may be substantially level with each other. Semiconductor strips **26** are between neighboring STI regions **24**. In accordance with some embodiments of the present disclosure, semiconductor strips **26** are parts of the original substrate **20**, and hence the material of semiconductor strips **26** is the same as that of substrate **20**. In accordance with alternative embodiments of the present disclosure, semiconductor strips **26** are replacement strips formed by etching the portions of substrate **20** between STI regions **24** to form recesses, and performing an epitaxy to regrow another semiconductor material in the recesses. Accordingly, semiconductor strips **26** are formed of a semiconductor material different from that of substrate **20**. In accordance with some embodiments, semiconductor strips **26** are formed of silicon germanium, silicon carbon, or a III-V compound semiconductor material. Hard masks **30** are then removed.

Referring to FIG. 3, STI regions **24** are recessed, so that the top portions of semiconductor strips **26** protrude higher than the top surfaces **24A** of the remaining portions of STI regions **24** to form protruding fins **36**. The respective process is illustrated as process **206** in the process flow **200** shown in FIG. **23**. Pad oxides **28** are also removed. The etching may be performed using a dry etching process, wherein HF and NH_3 , for example, are used as the etching gases. During the etching process, plasma may be generated. Argon may also be included. In accordance with alternative embodiments of the present disclosure, the recessing of STI regions **24** is performed using a wet etch process. The etching chemical may include HF, for example.

In above-illustrated embodiments, the fins may be patterned by any suitable method. For example, the fins may be patterned using one or more photolithography processes, including double-patterning or multi-patterning processes. Generally, double-patterning or multi-patterning processes combine photolithography and self-aligned processes, allowing patterns to be created that have, for example, pitches smaller than what is otherwise obtainable using a single, direct photolithography process. For example, in one embodiment, a sacrificial layer is formed over a substrate and patterned using a photolithography process. Spacers are formed alongside the patterned sacrificial layer using a self-aligned process. The sacrificial layer is then removed, and the remaining spacers, or mandrels, may then be used to pattern the fins.

Referring to FIG. 4, dummy gate stacks **38** are formed to extend on the top surfaces and the sidewalls of (protruding) fins **36**. The respective process is illustrated as process **208** in the process flow **200** shown in FIG. **23**. Dummy gate stacks **38** may include dummy gate dielectrics **40** and dummy gate electrodes **42** over dummy gate dielectrics **40**. Dummy gate dielectrics **40** may be formed of silicon oxide or like materials. Dummy gate electrodes **42** may be formed, for example, using polysilicon, and other materials may also be used. Each of dummy gate stacks **38** may also include one (or a plurality of) hard mask layer **44** over dummy gate electrodes **42**. Hard mask layers **44** may be formed of silicon nitride, silicon oxide, silicon carbo-nitride, or multi-layers thereof. Dummy gate stacks **38** may cross over a single one

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or a plurality of protruding fins **36** and/or STI regions **24**. Dummy gate stacks **38** also have lengthwise directions perpendicular to the lengthwise directions of protruding fins **36**.

Next, gate spacers **46** are formed on the sidewalls of dummy gate stacks **38**. The respective process is also shown as process **208** in the process flow **200** shown in FIG. **23**. In accordance with some embodiments of the present disclosure, gate spacers **46** are formed of a low-k dielectric material(s) such as porous silicon oxynitride, porous silicon carbo-nitride, porous silicon nitride, or the like, and may have a single-layer structure or a multi-layer structure including a plurality of dielectric layers. The dielectric constant (k value) of gate spacers **46** is lower than 3.8, and may be lower than about 3.0, for example, in the range between about 2.5 and about 3.0.

An etching process is then performed to etch the portions of protruding fins **36** that are not covered by dummy gate stacks **38** and gate spacers **46**, resulting in the structure shown in FIG. **5**. The respective process is illustrated as process **210** in the process flow **200** shown in FIG. **23**. The recessing may be anisotropic, and hence the portions of fins **36** directly underlying dummy gate stacks **38** and gate spacers **46** are protected, and are not etched. The top surfaces of the recessed semiconductor strips **26** may be lower than the top surfaces **24A** of STI regions **24** in accordance with some embodiments. Recesses **50** are accordingly formed. Recesses **50** comprise portions located on the opposite sides of dummy gate stacks **38**, and portions

remaining portions of protruding fins **36**. Next, epitaxy regions (source/drain regions) **54** are formed by selectively growing (through epitaxy) a semiconductor material in recesses **50**, resulting in the structure in FIG. **6**. The respective process is illustrated as process **212** in the process flow **200** shown in FIG. **23**. Depending on whether the resulting FinFET is a p-type FinFET or an n-type FinFET, a p-type or an n-type impurity may be in-situ doped with the proceeding of the epitaxy. For example, when the resulting FinFET is a p-type FinFET, silicon germanium boron (SiGeB), silicon boron (SiB), or the like may be grown. Conversely, when the resulting FinFET is an n-type FinFET, silicon phosphorous (SiP), silicon carbon phosphorous (SiCP), or the like may be grown. In accordance with alternative embodiments of the present disclosure, epitaxy regions **54** comprise III-V compound semiconductors such as GaAs, InP, GaN, InGaAs, InAlAs, GaSb, AlSb, AlAs, AlP, GaP, combinations thereof, or multi-layers thereof. After Recesses **50** are filled with epitaxy regions **54**, the further epitaxial growth of epitaxy regions **54** causes epitaxy regions **54** to expand horizontally, and facets may be formed. The further growth of epitaxy regions **54** may also cause neighboring epitaxy regions **54** to merge with each other. Voids (air gaps) **56** may be generated. In accordance with some embodiments of the present disclosure, the formation of epitaxy regions **54** may be finished when the top surface of epitaxy regions **54** is still wavy, or when the top surface of the merged epitaxy regions **54** has become planar, which is achieved by further growing on the epitaxy regions **54** as shown in FIG. **6**.

After the epitaxy step, epitaxy regions **54** may be further implanted with a p-type or an n-type impurity to form source and drain regions, which are also denoted using reference numeral **54**. In accordance with alternative embodiments of the present disclosure, the implantation step is skipped when epitaxy regions **54** are in-situ doped with the p-type or n-type impurity during the epitaxy.

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FIG. **7A** illustrates a perspective view of the structure after the formation of Contact Etch Stop Layer (CESL) **58** and Inter-Layer Dielectric (ILD) **60**. The respective process is illustrated as process **214** in the process flow **200** shown in FIG. **23**. CESL **58** may be formed of silicon nitride, silicon oxide, silicon carbo-nitride, or the like, and may be formed using CVD, ALD, or the like. ILD **60** may include a dielectric material formed using, for example, FCVD, spin-on coating, CVD, or another deposition method. ILD **60** may be formed of an oxygen-containing dielectric material, which may be a silicon-oxide based material such as silicon oxide, Phospho-Silicate Glass (PSG), Boro-Silicate Glass (BSG), Boron-Doped Phospho-Silicate Glass (BPSG), or the like. A planarization process such as a CMP process or a mechanical grinding process may be performed to level the top surfaces of ILD **60**, dummy gate stacks **38**, and gate spacers **46** with each other. FIG. **7B** illustrates the reference cross-section **7B-7B** as shown in FIG. **7A** in accordance with some embodiments, with one dummy gate stacks **38** illustrated.

After the structures shown in FIGS. **7A** and **7B** are formed, the dummy gate stacks **38** are replaced with metal gates and replacement gate dielectrics, as shown in FIGS. **8A**, **8B** and **9-12**. In subsequent figures, the top surfaces **24A** of STI regions **24** are illustrated to show the position of semiconductor fin **36**, which protrudes higher than top surfaces **24A** of STI regions **24**.

To form the replacement gates, hard mask layer **44**, dummy gate electrode **42**, and dummy gate dielectric **40** as shown in FIG. **7B** are removed first, forming openings **59** as shown in FIGS. **8A** and **8B**. The respective process is illustrated as process **216** in the process flow **200** shown in FIG. **23**. The top surface and the sidewalls of protruding fin **36** are exposed to openings **59**.

Next, referring to FIG. **9**, gate dielectric **61** is formed, which extends into openings **59**. The respective process is illustrated as process **218** in the process flow **200** shown in FIG. **23**. In accordance with some embodiments of the present disclosure, gate dielectric **61** includes Interfacial Layer (IL) **62**, which is formed on the exposed top surface and sidewall surfaces of protruding fin **36**. ILs **62** may include an oxide layer such as a silicon oxide layer, which is formed through the thermal oxidation of a surface portion of protruding fin **36**, a chemical oxidation process, or a deposition process. The gate dielectric **61** may also include high-k dielectric layer **64** over IL **62**. High-k dielectric layer **64** may be formed of a high-k dielectric material such as hafnium oxide, lanthanum oxide, aluminum oxide, zirconium oxide, combinations thereof, multi-layers thereof, or the like. The dielectric constant (k-value) of the high-k dielectric material is higher than 3.9, and may be higher than about 7.0, and sometimes as high as 21.0 or higher. High-k dielectric layer **64** is overlying, and may contact, IL **62**. High-k dielectric layer **64** is formed as a conformal layer, and extends on the sidewalls of protruding fin **36** and the top surface and the sidewalls of gate spacers **46**. In accordance with some embodiments of the present disclosure, high-k dielectric layer **64** is formed using ALD, CVD, or the like.

In accordance some embodiments, an adhesion layer (which is also a diffusion barrier layer) **65** is formed over high-k dielectric layer **64**. The respective process is illustrated as process **220** in the process flow **200** shown in FIG. **23**. Adhesion layer **65** may be formed of TiN or Titanium Silicon Nitride (TSN). The TiN layer may be formed using ALD or CVD, and the TSN layer may include alternately deposited TiN layers and SiN layers, which are formed using ALD, for example. Since the TiN layers and SiN layers are

very thin, these layers may not be able to be distinguished from each other, and are hence referred to as a TSN layer. In accordance with alternative embodiments, adhesion layer **65** is not formed, and the subsequently formed work-function layer is in contact with high-k dielectric layer **64**. Accordingly, the process **220** in FIG. **23** is shown using a dashed box to indicate it may be performed or may be skipped. In subsequent figures, adhesion layer **65** is not shown, while it may or may not be formed.

Referring to FIGS. **10** and **11**, work-function layer **66** is formed through deposition. The respective process is illustrated as process **222** in the process flow **200** shown in FIG. **23**. Work-function layer **66** includes at least one homogeneous layer (such as sub layer **66A** in FIG. **10**) having an entirety formed of a same material, or may include a plurality of sub layers formed of materials different from each other. The materials of the layer(s) in work-function layer **66** may be selected according to whether the respective FinFET formed is an n-type FinFET or a p-type FinFET. For example, when the FinFET is an n-type FinFET, work-function layer **66** may include an n-work-function layer, which may be Al-based layer (formed of, for example, TiAl, TiAlN, TiAlC, TaAlN, TaAl, TaAlC, or the like), or multi-layers thereof. If the adhesion layer **65** is not formed, a titanium nitride (TiN) layer (not shown) may or may not be formed between (and contacting) the n-work-function layer and high-k dielectric layer **64** to tune the work function. When the FinFET is a p-type FinFET, the corresponding work-function layer **66** may include a p-work-function layer such as a TiN layer, a tungsten carbon nitride (WCN) layer, or the like.

In accordance with some embodiments, work function layer **66** may include sub layer **66A** and sub layer **66B**, as shown in FIG. **11**. For example, a work function layer **66** of an n-type FinFET may include an n-work-function layer (represented as **66A**) and a p-work-function layer (represented as **66B**) over the n-work-function layer, wherein the n-work-function layer dominates the work function of the respective FinFET, and the p-work-function layer is formed simultaneously when the p-work-function layer is formed for a p-type FinFET.

In accordance with alternative embodiments, as shown in FIG. **11**, a work function layer of a p-type FinFET may also include a p-work-function layer (represented as **66A**) and an n-work-function layer (represented as **66B**) over the p-work-function layer, wherein the p-work-function layer dominates the work function of the respective FinFET, and the n-work-function layer is formed simultaneously when the n-work-function layer is formed for an n-type FinFET. In subsequent example figures, both work function layers **66A** and **66B** are shown, while a single work function layer may be used instead in accordance with some embodiments.

In accordance with some embodiments of the present disclosure, blocking layer **70** (which is an adhesion layer) is formed over work-function layer **66**. The respective process is illustrated as process **224** in the process flow **200** shown in FIG. **23**. Blocking layer **70** may be a metal-containing layer, which may be formed of TiN in accordance with some embodiments. Other materials such as TaN may also be used. In accordance with some embodiments, blocking layer **70** is formed using ALD, CVD, or the like. In accordance with some embodiments, glue layer **70** fully fills the remaining opening **59** (FIG. **8B**). In accordance with alternative embodiments, a gap-filling process is performed to fill the remaining opening **59** with a filling metal, which may be formed of tungsten, cobalt, or the like.

After opening **59** is fully filled, a planarization process such a Chemical Mechanical Polish (CMP) process or a mechanical polish process is performed to remove excess portions of the deposited layers as shown in FIG. **11**, resulting in the gate stack **76** as shown in FIG. **12**. The respective process is illustrated as process **226** in the process flow **200** shown in FIG. **23**. Gate stack **76** includes gate dielectric **61** and gate electrode **74**.

FIGS. **13** and **14** illustrate the processes for recessing gate stack **76**. The respective process is illustrated as process **228** in the process flow **200** shown in FIG. **23**. FIG. **13** illustrates a first etch-back process **78** performed on gate stack **76** and gate spacers **46**, wherein the etching is represented by arrows. Recess **80** is generated accordingly. The first etch-back process may include a dry etch process and/or a wet etch process. Furthermore, the etching may be isotropic or anisotropic. In accordance with some embodiments of the present disclosure, the first etch-back process is performed using an etchant that etches gate spacers **46** and gate stack **76**, and does not etch CESL **58** and ILD **60**. In accordance with some embodiments when a dry etching process is used, the etching gases includes a fluorine-based etchant such as CF_4 , C_2F_6 , NF_3 , or the like, or combinations thereof. In accordance with some embodiments when a wet etching process is used, the etching chemical may include diluted HF solution, NH_4OH (ammonia solution), or combinations thereof. In accordance with some embodiments, after the first etch-back process, the height of gate stacks **76** is H_1 , which may be in the range between about 10 nm and about 40 nm. The vertical distance from the top surface of protruding fins **36** to the top surface of ILD **60** is represented as H_2 . The ratio H_1/H_2 may be in the range between about 1/3 and about 1/2. The recessing depth D_1 may be in the range between about 50 nm and about 80 nm. It is appreciated that the value of recessing depth D_1 cannot be too high or too low. If the value is too high, some parts (such as the parts directly over protruding fin **36**) of gate stack **76** may be adversely removed, causing device failure. If the value is too low, not enough recess is generated to accommodate the self-aligned hard mask in subsequent processes.

In accordance with some embodiments as shown in FIG. **13**, gate spacers **46** are recessed by the first etch-back process **78**. In accordance with alternative embodiments, gate spacers **46** are not recessed by the first etch-back process **78**, wherein dashed lines **46'** are illustrated to show the top portions of gate spacers **46** that remain after the first etch-back process.

After the first etch-back process as shown in FIG. **13**, a second etch-back process **78'** may be performed, as shown in FIG. **14**. Recess **81** is thus formed between the opposing portions of the corresponding high-k dielectric layer **64**. The second etch-back process **78'** is performed using an etching gas or an etching chemical solution different from that is used in the first etch-back process **78**. The second etch-back process **78'** may include a dry etch process and/or a wet etch process. Furthermore, the etching may be isotropic or anisotropic. In accordance with some embodiments of the present disclosure, the second etch-back process is performed using an etchant that etches gate electrode **74**, and does not etch gate spacers **46**, high-k dielectric layer **64**, CESL **58**, and ILD **60**. In accordance with some embodiments when a dry etching process is used, the etching gases may include BCl_3 , Cl_2 , WF_6 , or combinations thereof. In accordance with some embodiments in which a wet etching process is used, the etching chemical may include NH_4OH or the like. In accordance with some embodiments, the recessing depth D_2 may be in the range between about 4 nm and about 8 nm. It is

appreciated that the value of recessing depth D2 also cannot be too high or too low. If the value is too high, some parts of gate electrode 74 may be adversely removed, causing device failure. If the value is too low, not enough recess is generated to accommodate the subsequent filling of low-resistivity conductive layers. In accordance with some embodiments, the height H3 of gate stack 76 after the second etch-back process 78' is in the range between about 5 nm and about 30 nm.

Due to the selectivity of the etchant on different materials, the top surface 46TS of gate spacers 46 may be level with, higher than, or lower than, the top surfaces 64TS of high-k dielectric layer 64.

FIG. 15 illustrates a passivation process 82 performed in accordance with some embodiments. The respective process is illustrated as process 230 in the process flow 200 shown in FIG. 23. In accordance with some embodiments when dry etching is used in the etching processes 78 and 78', the material of gate electrode 74 may be re-sputtered onto high-k dielectric layer 64, gate spacers 46, CESL 58, and ILD 60. This may result in some problems. For example, the re-sputtered materials become the seed layer for the subsequently selectively deposited low-resistivity layers 84A and 84B (FIG. 18), causing low-resistivity layers 84A and 84B to be grown to undesirable places. Also, these materials may cause the electrical shorting between gate electrode 74 and other conductive features such as contact plugs 94 (FIG. 20A). Accordingly, a passivation process is performed to improve selectivity in the subsequent deposition processes, and to convert the re-sputtered materials (if any) into dielectric materials. In accordance with other embodiments, passivation process 82 is skipped when the re-sputter is not severe enough to affect the selectivity in deposition. Accordingly, passivation process 230 is illustrated using a dashed box in FIG. 23.

In accordance with some embodiments, the passivation process 82 is performed by annealing wafer 10 in an oxygen (O₂) containing environment, or performing a plasma treatment on wafer 10 using O₂ as a process gas. In accordance with some embodiments, the oxygen annealing is performed at a temperature in the range between about 200° C. and about 350° C., for a period of time, for example, in a range between about 10 secs and about 60 seconds. As a result, a surface layer of gate electrode 74 and the re-sputtered material will be oxidized to form an oxide. In accordance with alternative embodiments, the passivation process 82 is performed by treating wafer 10 in a nitrogen (N₂) and hydrogen (H₂) containing environment. As a result, a surface layer of gate electrode 74 and the re-sputtered material will be converted into a nitride. It is appreciated that gate electrode 74 may already comprise a metal nitride, and the nitriding will still improve selectivity because the damaged sidewall of SiN is passivated, and also the metal residue is passivated so that the selectivity is improved. In accordance with yet alternative embodiments, the passivation process 82 is performed by thermal-soaking wafer 10 in an NF₃ containing environment, or performing a plasma treatment on wafer 10 using NF₃ as a process gas. In accordance with some embodiments, the thermal soaking is performed at a temperature in the range between about 250° C. and about 400° C., for a period of time, for example, in a range between about 1 minute and about 10 minutes.

Referring to FIG. 16, a first low-resistivity conductive layer 84A, which may be a metal layer, is formed using a selective deposition process. Low-resistivity conductive layer 84A is also referred to as bottom sub (metal) layer 84A hereinafter. The respective process is illustrated as process

232 in the process flow 200 shown in FIG. 23. Throughout the description, bottom sub layer 84A may also be considered as parts of the respective gate electrodes. In accordance with some embodiments of the present disclosure, bottom sub layer 84A is formed of tungsten (W). The resistivity of the bottom sub layer 84A may be lower than the resistivity of the layers (which include layers 66 and 70) in gate electrode 74. Bottom sub layer 84A is formed on gate electrode 74, and not on the exposed surfaces of dielectric materials including gate spacers 46, high-k dielectric layer 64, CESL 58, and ILD 60. In accordance with some embodiments, the deposition is performed using ALD. The precursor may include WCl₅ and a reducing agent such as H₂. The deposition process includes a plurality of ALD cycles, each including conducting WCl₅, purging WCl₅, conducting H₂, and purging H₂. The deposition process may be performed at an elevated temperature, such as in the range between about 400° C. and about 500° C.

It is appreciated that WCl₅ has the function of etching metal oxides. Accordingly, if the first passivation process 82 is performed using oxygen, the resulting metal oxide formed due to the oxidation of the surface layer of gate electrode 74 and the re-sputter material of gate electrode 74 are etched before bottom sub layer 84A is grown.

Referring to FIG. 17, after the bottom sub layer 84A is deposited, passivation process 86 is performed. The respective process is illustrated as process 234 in the process flow 200 shown in FIG. 23. In accordance with alternative embodiments, passivation process 86 is skipped. Accordingly, the step 234 in FIG. 23 is illustrated using a dashed box to indicate it may be performed or skipped. Passivation process 86 may be performed using a method and a process gas selected from the same candidate group of methods and process gases for passivation process 82 (FIG. 15). Accordingly, the details are not repeated herein. Furthermore, the passivation process 86 may be performed using the same method and process gases or different methods and process gases.

Referring to FIG. 18, after the formation of bottom sub layer 84A and the possible passivation process 86, metal layer 84B (referred to as top sub (metal) layer 84B hereinafter) is selectively deposited on bottom sub layer 84A. The respective process is illustrated as process 236 in the process flow 200 shown in FIG. 23. The resistivity of the top sub layer 84B is also lower than the resistivity of the layers (which include layers 66 and 70) in gate electrode 74. Top sub layer 84B is formed using bottom sub layer 84A as a seed layer, and hence is not deposited on the exposed surfaces of dielectric materials such as gate spacers 46, high-k dielectric layer 64, CESL 58, and ILD 60. In accordance with some embodiments, the deposition of top sub layer 84B is performed using ALD. The precursor is different from the precursor for depositing bottom sub layer 84A. For example, the precursor for forming top sub layer 84B may include WF₆ and a reducing agent such as H₂. The process may include a plurality of ALD cycles, each including conducting WF₆, purging WF₆, conducting H₂, and purging H₂. The deposition process may be a thermal process performed at an elevated temperature, such as in the range between about 250° C. and about 400° C.

Sub layers 84A and 84B have different functions. Bottom sub layer 84A (which may be formed using WCl₅) is able to be selectively grown on gate electrode 74 (such as TiN) without being deposited on the exposed dielectric layers. However, bottom sub layer 84A cannot be deposited to be too thick because with the continued deposition of bottom sub layer 84A, it will eventually be deposited on the exposed

dielectric layers. Accordingly, the deposition of bottom sub layer **84A** is stopped before it starts to be deposited on the exposed dielectric layers. In accordance with some embodiments, the thickness of bottom sub layer **84A** is smaller than about 3 nm to ensure it is not deposited on the exposed dielectric layers. On the other hand, bottom sub layer **84A** is used as a seed layer for the selective growth of top sub layer **84B**, which does not grow on gate electrode **74**. Bottom sub layer **84A** thus has a high-enough thickness to ensure it fully covers the exposed gate electrode **74**, and hence the thickness of bottom sub layer **84A** is greater than about 1 nm. Accordingly, the thickness **T1** of bottom sub layer **84A** may be in the range between about 1 nm and about 3 nm.

Top sub layer **84B** (which may be formed using WF_6) is deposited on metal such as bottom sub layer **84A**, and is not deposited on the exposed dielectric layer, even if the deposition of top sub layer **84B** lasts for a long period of time. Accordingly, with the bottom sub layer **84A** being formed as the seed layer, top sub layer **84B** is selectively deposited on bottom sub layer **84A**. When the thickness **T2** of top sub layer **84B** is high, it still does not grow on the exposed dielectric layers. Accordingly, the thickness **T2** of top sub layer **84B** may be increased without the concern of being grown on the exposed dielectric layers. The thickness **T2** of top sub layer **84B** may be greater than about 1 nm, and may be greater than about 3 nm, greater than about 5 nm, or greater. In accordance with some embodiments, thickness **T2** is in the range between about 1 nm and about 5 nm. The top surface of top sub layer **84B** may be level with or slightly lower than the top ends of high-k dielectric layer **64**. Bottom sub layers **84A** and top sub layers **84B** are collectively referred to as low-resistivity conductive layer **84**. Throughout the description, low-resistivity conductive layer **84** is considered as a part of gate electrode, which is denoted as **74'**. Low-resistivity conductive layers **84A** and **84B** in combination may reach a high-enough thickness and hence the overall resistivity of gate electrode **74** (which includes low-resistivity conductive layer **84**) may be reduced.

Due to the selective deposition, sub layers **84A** and **84B** may be conformal layers. Furthermore, sub layers **84A** and **84B** may be substantially planar if the top surface of the underlying portion of gate electrode **74'** is planar. Alternatively, sub layers **84A** and **84B** are curved and have the topology following the top-surface profile of the respective underlying portions of gate electrode **74'**.

Next, referring to FIG. **19**, the remaining recesses **80** and **81** (if any) are filled with a dielectric material to form self-aligned hard mask **88**. The respective process is illustrated as process **238** in the process flow **200** shown in FIG. **23**. Self-aligned hard mask **88** may be formed of a non-low-k dielectric material such as silicon nitride, silicon oxynitride, silicon oxy-carbide, or the like. Self-aligned hard mask **88** may also be formed of a homogeneous low-k dielectric material, which may be formed of porous silicon nitride, porous silicon oxynitride, porous silicon oxy-carbide, or the like. Self-aligned hard mask **88** is also planarized so that its top surface is coplanar with the top surface of ILD **60**. In accordance with some embodiments, the sidewalls of self-aligned hard mask **88** are in contact with the sidewalls of CESL **58**. In accordance with other embodiments in which gate spacers **46** are not recessed, the sidewalls of self-aligned hard mask **88** are in contact with the sidewalls of the top portions (illustrated as dashed lines **46'**) of gate spacers **46**.

FIG. **20A** illustrates the formation of gate contact plug **90**, source/drain silicide regions **92**, and source/drain contact plugs **94**. The respective process is illustrated as process **240**

in the process flow **200** shown in FIG. **23**. The formation of source/drain contact plugs **94** includes forming contact openings by etching ILD **60** to expose the underlying portions of CESL **58**, and then etching the exposed portions of CESL **58** to reveal source/drain regions **54**. In a subsequent process, a metal layer (such as a titanium layer) is deposited to extend into the contact openings. A metal nitride blocking layer (such as a TiN layer) may be formed. An anneal process is then performed to react the metal layer with the top portion of source/drain regions **54** to form silicide regions **92**. Next, either the previously formed metal nitride layer is left without being removed, or the previously formed metal nitride layer is removed, followed by the deposition of a new metal nitride layer (such as a titanium nitride layer). A filling metallic material such as tungsten, cobalt, or the like, is then filled into the contact openings, followed by a planarization process to remove excess materials, resulting in source/drain contact plugs **94**. The formation of gate contact plug **90** may include etching self-aligned hard mask **88** to reveal top sub layer **84B**, and forming gate contact plug **90** in the corresponding openings. Gate contact plug **90** may also include a diffusion barrier layer (such as titanium nitride) and a metal (such as copper, tungsten, cobalt, or the like) over the diffusion barrier layer. FinFET **100** is thus formed. FIG. **20B** illustrates a perspective view of FinFET **100**.

In FIG. **20A**, thickness ratio $T2/T1$ is designed to be in a range that is not too big and not small. When the ratio $T2/T1$ is too big, either thickness **T1** is too small, and/or thickness **T2** is too big. If thickness **T1** is too small, bottom sub layer **84A** may not be able to fully cover gate electrode **66**, and cannot function as an effective seed layer. If thickness **T2** is too big, the top surface of the top sub layer **84B** may be higher than the top ends of high-k dielectric layer **64**, causing problems for the subsequent formation of self-aligned hard mask **88**. On the other hand, when the ratio $T2/T1$ is too small, either thickness **T1** is too big, and/or thickness **T2** is too small. If thickness **T1** is too big, bottom sub layer **84A** may be grown on dielectric materials such as ILD **60**, and the deposition of bottom sub layer **84A** and top sub layer **84B** is not selective. If thickness **T2** is too small, the resistance of layer **84B** (and hence the total resistance of layers **84A** and **84B**) is high, defeating the purpose of forming the low-resistivity conductive layers **84A** and **84B**. In accordance with some embodiments, ratio $T2/T1$ is in the range between 1 and about 5.

To ensure that top sub layer **84B** does not grow on top of high-k dielectric layer **64** and gate spacers **46**, the top surface of top sub layer **84B** may be level with the top ends of high-k dielectric layer **64** and/or the top ends of gate spacers **46** in accordance with some embodiments. In accordance with alternative embodiments, the top surface of top sub layer **84B** is lower than the top ends of high-k dielectric layer **64** and/or the top ends of gate spacers **46** by a difference to provide a process margin. The difference may be smaller than about 1 nm.

As shown in FIG. **20A**, the bottom surface of gate contact plug **90** may extend from the illustrated left edge to the illustrated right edge of top sub layer **84B**. Alternatively, the bottom surface of gate contact plug **90** may be laterally recessed from the left edge and/or the right edge of top sub layer **84B**, as illustrated in FIG. **20A**. In accordance with yet alternative embodiments, the bottom surface of gate contact plug **90** may extend on and contact the top ends of high-k dielectric layer, and may, or may not, extend on and contact the top ends of gate spacers **46**.

FIG. 21 illustrates a top view of some portions of FinFET 100. Gate electrode 74' and the overlying low-resistivity conductive layers 84A and 84B. The vertical portions of high-k dielectric layer 64 may form rings encircling the corresponding gate electrode 74' (including the corresponding overlying low-resistivity conductive layer 84). Gate contact plug 90, protruding fins 36, and source/drain regions 54 are also illustrated.

As shown in FIG. 21, low-resistivity conductive layers 84A and 84B may fully overlap work function layer 66, and the edges of conductive layers 84A and 84B may be flushed with the corresponding edges of work function layer 66. High-k gate dielectric 64 may form a ring contacting the sidewalls of low-resistivity conductive layers 84A and 84B and work function layer 66. Hard mask 88 may be fully encircled by the vertical portions of CESL 58. Gate contact plug 90 may contact a portion, and not all, of top sub layer 84B, with low-resistivity conductive layers 84A and 84B extending beyond the left sidewall 90C and the right sidewall 90D of gate contact plug 90. It is appreciated that although the sidewalls 90A and 90B of gate contact plug 90 are shown as being directly on top sub layer 84B, sidewalls 90A and 90B may extend in the direction of arrows 95 and may be at any position on the paths of arrows 95.

FIG. 22 illustrates the schematic distribution of some elements, wherein the atomic percentages of elements F, Cl, and N are illustrated as a function of the height in gate electrode 74, wherein the height is measured in the direction of arrow 108 in FIG. 20A. Lines 102, 104, and 106 illustrate the example atomic percentages of chlorine, fluorine, and nitrogen, respectively. As shown by line 102, when bottom sub layer 84A is formed adopting WCl_5 as a process gas, the peak atomic percentage of Cl is in bottom sub layer 84A, and the Cl atomic percentage reduces gradually in top sub layer 84B (and dielectric hard mask 88) and work function layer 66. As shown by line 104, since top sub layer 84B may be formed adopting WF_6 as a process gas, the peak atomic percentage of F is in top sub layer 84B, and the F atomic percentage reduces gradually in bottom sub layer 84A and dielectric hard mask 88 and gate contact plug 90. The distribution of lines 102 and 104 may be observed using X-ray photoelectron spectroscopy (XPS). In accordance with some embodiments, the peak atomic percentage of F in top sub layer 84B is higher than about 12 percent, and may be in the range between about 5 percent and about 20 percent. The peak atomic percentage of Cl in bottom sub layer 84A is higher than about 10 percent, and may be in the range between about 5 percent and about 20 percent.

Line 106 illustrates an embodiment in which passivation process 86 is performed using N_2 after the deposition of layer 84A and before the deposition of layer 84B. In accordance with some embodiments, a peak nitrogen atomic percentage is at the interface between layers 84A and 84B, and the nitrogen atomic percentage dips in both of sub layers 84A and 84B. The distribution of line 106 may be observed using Energy Dispersive X-Ray Spectroscopy (EDS or EDX). Also, the two layers 84A and 84B may be distinguished from each other using EDX. Experiments also revealed that sub layers 84A and 84B may be distinguished from each other using Transmission electron microscopy (TEM) due to their crystallinity difference.

The embodiments of the present disclosure have some advantageous features. By forming a first low-resistivity conductive layer, it is possible to achieve the selective deposition of the first low-resistivity conductive layer on gate electrode, and not on the exposed dielectric layers. The loss of selectivity due to the prolonged disposition of the

low-resistivity conductive layer is solved by stopping the deposition of the first low-resistivity conductive layer, and depositing a second low-resistivity conductive layer that is selectively deposited on metal. The selectivity is deposition is not lost when the thickness of the second low-resistivity conductive layer is increased.

In accordance with some embodiments of the present disclosure, a method comprises forming a gate electrode on a semiconductor region; recessing the gate electrode to generate a recess; performing a first deposition process to form a first metallic layer on the gate electrode and in the recess, wherein the first deposition process is performed using a first precursor; performing a second deposition process to form a second metallic layer on the first metallic layer using a second precursor different from the first precursor, wherein the first metallic layer and the second metallic layer comprise a same metal; forming a dielectric hard mask over the second metallic layer; and forming a gate contact plug penetrating through the dielectric hard mask, wherein the gate contact plug contacts a top surface of the second metallic layer. In an embodiment, the first precursor comprises tungsten chloride (WCl_5), and the second precursor comprises tungsten fluoride (WF_6). In an embodiment, in the first deposition process, surfaces of dielectric materials adjacent to the gate electrode are exposed, and the first deposition process is stopped before the first metal layer starts growing on exposed dielectric materials adjacent to the gate electrode. In an embodiment, each of the first deposition process and the second deposition process comprises an atomic layer deposition process. In an embodiment, the recessing the gate electrode comprises a first recessing process to recess the gate electrode, a gate dielectric, and gate spacers, wherein the gate dielectric comprises first sidewall portions on sidewalls of the gate electrode, and the gate electrode and the gate dielectric are between the gate spacers; and a second recessing process to recess the gate electrode to be lower than top edges of the gate dielectric. In an embodiment, the first metallic layer has a first thickness smaller than about 3 nm. In an embodiment, the second metallic layer has a second thickness greater than about 3 nm.

In accordance with some embodiments of the present disclosure, a device includes a semiconductor region; a gate dielectric over the semiconductor region; a gate electrode comprising a first portion comprising a work-function layer therein; and a second portion overlying and contacting the first portion, wherein the second portion comprises fluorine and chlorine, and wherein the second portion comprises a bottom sub layer, wherein a first peak atomic percentage of chlorine is in the bottom sub layer; and a top sub layer over and contacting the bottom sub layer, wherein a second peak atomic percentage of fluorine is in the top sub layer, and wherein the bottom sub layer and the top sub layer comprise a same metal; and a gate contact plug over and contacting the top sub layer. In an embodiment, the first portion comprises titanium, and the second portion comprises tungsten. In an embodiment, the bottom sub layer and the top sub layer are distinguishable through Transmission electron microscopy (TEM). In an embodiment, the gate dielectric comprises sidewall portions, and a bottom portion underlying and connected to the sidewall portions, and wherein the first portion and the second portion of the gate electrode are between the sidewall portions. In an embodiment, a top surface of the top sub layer is level with or lower than top edges of the sidewall portions of the gate dielectric. In an embodiment, the device further comprises gate spacers on opposing sides of the gate dielectric and the gate electrode;

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and an inter-layer dielectric, with the gate spacers in the inter-layer dielectric, wherein a first top surface of the gate dielectric is recessed lower than a second top surface of the inter-layer dielectric. In an embodiment, the gate spacers are recessed to have a third top surface lower than the second top surface.

In accordance with some embodiments of the present disclosure, a device includes a semiconductor substrate; isolation regions extending into the semiconductor substrate; a semiconductor fin protruding higher than portions of the isolation regions on opposing sides of the semiconductor fin; and a gate stack comprising a high-k gate dielectric on the semiconductor fin; a work function layer on the high-k gate dielectric; a capping layer; a first tungsten layer over and contacting the work function layer and the capping layer; and a second tungsten layer over and contacting the first tungsten layer, wherein the first tungsten layer and the second tungsten layer are distinguishable from each other. In an embodiment, both of the first tungsten layer and the second tungsten layer comprise fluorine and chlorine, and wherein a first peak atomic percentage of chlorine is in the first tungsten layer. In an embodiment, a second peak atomic percentage of fluorine is in the second tungsten layer. In an embodiment, both of the first tungsten layer and the second tungsten layer comprise nitrogen, and wherein nitrogen atomic percentages in the gate stack has a peak at an interface between the first tungsten layer and the second tungsten layer. In an embodiment, the high-k gate dielectric comprises sidewall portions on opposing sides of the first tungsten layer and the second tungsten layer, and a top surface of the second tungsten layer is between, and is level with or lower than top edges of the sidewall portions of the high-k gate dielectric. In an embodiment, the capping layer comprises titanium nitride.

The foregoing outlines features of several embodiments so that those skilled in the art may better understand the aspects of the present disclosure. Those skilled in the art should appreciate that they may readily use the present disclosure as a basis for designing or modifying other processes and structures for carrying out the same purposes and/or achieving the same advantages of the embodiments introduced herein. Those skilled in the art should also realize that such equivalent constructions do not depart from the spirit and scope of the present disclosure, and that they may make various changes, substitutions, and alterations herein without departing from the spirit and scope of the present disclosure.

What is claimed is:

1. A device comprising:

a semiconductor region;

a gate dielectric over the semiconductor region;

a recessed metal gate electrode comprising:

a first portion comprising a work-function layer therein; and

a second portion overlying and contacting the first portion, wherein the second portion comprises fluorine and chlorine, and wherein the second portion comprises:

a bottom sub layer, wherein a first peak atomic percentage of chlorine is in the bottom sub layer; and

a top sub layer over and contacting the bottom sub layer, wherein a second peak atomic percentage of fluorine is in the top sub layer, and wherein the bottom sub layer and the top sub layer comprise a same metal; and

a gate contact plug over and contacting the top sub layer.

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2. The device of claim 1, wherein the first portion comprises titanium, and the second portion comprises tungsten.

3. The device of claim 1, wherein the bottom sub layer and the top sub layer are distinguishable through Transmission electron microscopy (TEM).

4. The device of claim 1, wherein the gate dielectric comprises sidewall portions, and a bottom portion underlying and connected to the sidewall portions, and wherein the first portion and the second portion of the recessed metal gate electrode are between the sidewall portions.

5. The device of claim 4, wherein a top surface of the top sub layer is level with or lower than top edges of the sidewall portions of the gate dielectric.

6. The device of claim 1 further comprising: gate spacers on opposing sides of the gate dielectric and the recessed metal gate electrode; and an inter-layer dielectric, with the gate spacers in the inter-layer dielectric, wherein a first top surface of the gate dielectric is recessed lower than a second top surface of the inter-layer dielectric.

7. The device of claim 6, wherein the gate spacers are recessed to have a third top surface lower than the second top surface.

8. A device comprising:

a semiconductor substrate;

isolation regions extending into the semiconductor substrate;

a semiconductor fin protruding higher than portions of the isolation regions on opposing sides of the semiconductor fin; and

a recessed metal gate stack comprising:

a high-k gate dielectric on the semiconductor fin;

a work function layer on the high-k gate dielectric;

a capping layer;

a first tungsten layer over and contacting the work function layer and the capping layer; and

a second tungsten layer over and contacting the first tungsten layer, wherein the first tungsten layer and the second tungsten layer are distinguishable from each other, wherein both of the first tungsten layer and the second tungsten layer comprise fluorine and chlorine, and wherein a first peak atomic percentage of chlorine is in the first tungsten layer.

9. The device of claim 8, wherein a second peak atomic percentage of fluorine is in the second tungsten layer.

10. The device of claim 8, wherein both of the first tungsten layer and the second tungsten layer comprise nitrogen, and wherein nitrogen atomic percentages in the recessed metal gate stack has a peak at an interface between the first tungsten layer and the second tungsten layer.

11. The device of claim 8, wherein the high-k gate dielectric comprises sidewall portions on opposing sides of the first tungsten layer and the second tungsten layer, and a top surface of the second tungsten layer is between, and is level with or lower than top edges of the sidewall portions of the high-k gate dielectric.

12. The device of claim 8, wherein the capping layer comprises titanium nitride.

13. The device of claim 8, wherein the first tungsten layer has a first thickness, and the second tungsten layer has a second thickness greater than the first thickness.

14. A device comprising:

a semiconductor region;

a gate dielectric comprising:

a bottom portion; and

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a first sidewall portion and a second sidewall portion over and connecting to a first end and a second end, respectively, of the bottom portion;
a recessed metal gate electrode over the bottom portion of the gate dielectric, wherein the recessed metal gate electrode is between the first sidewall portion and the second sidewall portion of the gate dielectric;
a first metallic layer over and contacting the recessed metal gate electrode;
a second metallic layer over and contacting the first metallic layer, wherein the first metallic layer has a higher atomic percentage of chlorine than the second metallic layer, and the second metallic layer has a higher atomic percentage of fluorine than the first metallic layer; and
a gate contact plug over the second metallic layer.
15. The device of claim **14**, wherein a peak atomic concentration of chlorine is in the first metallic layer.

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16. The device of claim **14**, wherein a peak atomic concentration of fluorine is in the second metallic layer.
17. The device of claim **14**, wherein the first metallic layer and the second metallic layer comprise a same metal.
18. The device of claim **14**, wherein the first sidewall portion and the second sidewall portion have first sidewalls contacting second sidewalls of the first metallic layer to form first vertical interfaces.
19. The device of claim **18**, wherein the first sidewalls further contact third sidewalls of the second metallic layer to form second vertical interfaces.
20. The device of claim **14**, wherein the first metallic layer has a first thickness smaller than about 3 nm, and the second metallic layer has a second thickness greater than about 3 nm.

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